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Deactivation of Cu / ZnO catalyst during dehydrogenation of methanol

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The deactivation of Cu/ZnO catalyst during methanol dehydrogenation to form methyl formate has been studied. The Cu/ZnO catalyst was seriously deactivated under the reaction conditions: various temperatures of 493, 523 and 553 K, atmospheric pressure and methanol GHSV of 3000 ml (STP)/g-cat h. The weight loss due to reduction of ZnO in the Cu/ZnO catalyst was monitored by a microbalance. X-ray induced Auger spectroscopy of $Zn(L_3M_{4,5}M_{4,5})$ showed the increase in the concentration of metallic Zn on the catalyst surface after the reaction. Temperature-programmed reduction (TPR) of the Cu/ZnO catalyst with methanol demonstrated that the reduction of ZnO in Cu/ZnO was suppressed by introduction of CO_2 into the stream of helium–methanol. As the concentration of CO_2 in the feed gas increased, the weight loss of the Cu/ZnO catalyst due to the reduction of ZnO decreased. The deactivation of the Cu/ZnO catalyst in the methanol dehydrogenation was also retarded by the addition of CO_2. In particular, oxygen injection into the reactant feed regenerated the Cu/ZnO catalyst deactivated during the reaction. Based on these observations, the cause of deactivation of the Cu/ZnO catalyst has been discussed.

Keywords: methanol dehydrogenation; deactivation of Cu/ZnO catalyst; reduction of ZnO; oxidant effect; regeneration of deactivated catalyst

1. Introduction

Methanol dehydrogenation to form methyl formate has drawn attention because it is an important method of separation, storage and transportation of synthesis gas [1]. In addition, methyl formate is an attractive intermediate for the production of numerous chemicals, such as formic acid, dimethyl formamide and acetic acid [2]. There have been many investigations on copper-containing catalysts for methanol dehydrogenation [3–6]. Although copper-containing catalysts showed good catalytic activities for this reaction, they suffered from deactivation [7–9]. Sodesawa et al. carried out methanol dehydrogenation on copper catalysts and observed that deactivations depend on the supports [8,10,11]. They proposed the sintering of copper as a main reason for deactivation. On the other hand, Tonner et al. suggested that formaldehyde deposition took place on the catalyst and inhibited methanol dehydrogenation [12].

As was reported, ZnO has been chosen for the support of copper catalysts because of its good activity and selectivity to methyl formate [13]. The copper catalyst supported on ZnO for methanol dehydrogenation was, however, mentioned to be more seriously deactivated than the catalysts on other supports [12,14]. The unusual deactivation of the Cu/ZnO system invoked the participation of the ZnO support in the catalytic reaction [15]. ZnO is known to form oxygen defects from the reaction with methanol and hydrogen [16–18]. We also observed that the reduction of ZnO was promoted in the presence of copper [19]. In this report, the redox properties of the ZnO support were found to be closely related to the reactivity of the catalyst. We present preliminary results on the deactivation of Cu/ZnO catalyst and the reduction of ZnO in Cu/ZnO catalyst in methanol dehydrogenation. Correlation of the reduction of ZnO in Cu/ZnO to the deactivation of the catalyst is also attempted.

2. Experimental

The Cu/ZnO catalyst was prepared by coprecipitation of metal acetates at pH 7. The precipitate was washed, filtered, dried in a vacuum oven and calcined at 723 K for 16 h. The elemental analysis of the sample by atomic absorption spectroscopy (Perkin-Elmer Co., 3030B AAS) gave CuO/ZnO weight ratio of 47/53. The surface area of the CuO/ZnO catalyst measured by BET apparatus (Micromeritics Co., ASAP 2000) was 22.16 m^2/g, and the copper surface area measured by N_2O titration [20] was 5.02 m^2/g.

The methanol dehydrogenation was conducted in a stainless steel reactor (1/4″ o.d. × 20 cm length, 200 mg catalyst) under the reaction conditions: various temperatures of 493, 513 and 543 K, atmospheric pressure and methanol GHSV of 3000 ml(STP)/g-cat h. Methanol was introduced by passing helium gas through a thermostated methanol saturator. The reactants and products were analyzed by an on-line GC (TCD detector, porapak Q column, 1/8″ o.d. × 10 ft length). The conversion of methanol and the selectivity to methyl formate were determined based on carbon number. The catalyst was reduced in situ at 573 K for 3 h by 5% H_2 in Ar (60 ml/min). The reactor was purged with helium until no Ar was detected from the purged gas. Then, the helium gas saturated with methanol was introduced into the reactor.

The weight change of the Cu/ZnO catalyst during the methanol dehydrogenation was monitored by a microbalance (Cahn Instruments, Inc., Cahn 2000). Catalysts (60 mg) were loaded on a sample pan and reduced in situ at 623 K for 1 h by 5% H_2 in Ar (2120 ml/min). Then, methanol was introduced at 523 K as described above (9.2% methanol in helium, total flow of 120 ml/min). Temperature-programmed reduction (TPR) of CuO/ZnO was performed in the flow of helium–methanol with programmed heating up to 673 K at the rate of 10 K/min. The weight changes of the catalyst were recorded from changing CO_2/methanol ratio in the helium gas.

The X-ray induced Auger spectra of Cu/ZnO (Surface Science, 2803-S spectroscopy) were recorded using an Al anode. The samples were prepared in a glove box to prevent them from exposing to air. The kinetic energy of Zn($L_3M_{4,5}M_{4,5}$) was determined with reference to the binding energy of ZnO($2p_{3/2}$) at 2021.8 eV.

3. Results and discussion

The Cu/ZnO catalyst used in the methanol dehydrogenation was seriously deactivated within 1 h as shown in fig. 1. The concentration of methanol in the feed gas was 15 mol% with total flow of 67 ml/min. The conversion of methanol, 45% after 15 min, dropped to 15% after 45 min at 513 K. The catalyst was steadily deactivated over 20 h. The deactivation occurs in a similar fashion regardless of the reaction temperatures being 493, 513 or 543 K. The selectivity to methyl formate was about 92% at 493 K and lowered as the temperature increased. The low selec-

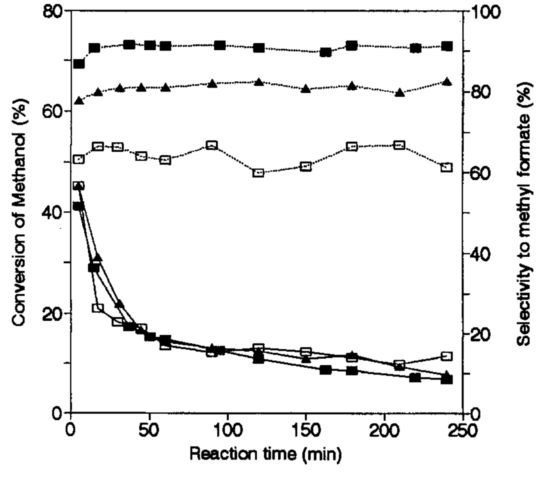

Fig. 1. Deactivation of Cu/ZnO catalyst in methanol dehydrogenation at 493 K (■), 523 K (▲) and 543 K (□): (——) conversion of methanol, (...) selectivity to methyl formate.

tivity to methyl formate at the higher temperature can be attributed to the decomposition of methyl formate into methanol and CO [21,22]. The selectivity slightly increased with reaction time.

Since the reduction of ZnO was promoted by the presence of copper in the vicinity [18], the reduction of ZnO in the Cu/ZnO catalyst with methanol was investigated with a microbalance. The catalyst sample was pretreated in situ with 5% H_2 in Ar to reduce CuO to metallic copper and purged with helium after cooling to 523 K. As shown in fig. 2, the catalyst weight steadily decreased during the reaction with methanol at 523 K. After 4 h, a 0.9% decrease of ZnO weight in the Cu/ZnO catalysts occurred, which is equivalent to the reduction of 4.4 mol% ZnO. The surface mole ratio to the bulk of ZnO was approximately calculated to be 0.034 [#1]. This result indicated that bulk ZnO was reduced from the reaction with methanol. The weight increase at the beginning of the reaction can be attributed to the adsorption of methanol onto the catalyst.

Along with the study on the reduction of bulk ZnO in the Cu/ZnO catalyst, the surface composition of ZnO was analyzed by X-ray photoelectron spectroscopy. Fig. 3 shows X-ray induced Auger spectra of $Zn(L_3M_{4,5}M_{4,5})$ in the catalyst samples, which were prepared under three different conditions: (a) calcined at 723 K for 16 h, (b) reduced at 623 K for 1 h by 5% H_2 in Ar after the calcination, (c) reacted with methanol at 523 K for 3 h after the calcination and reduction. All three samples show major peaks at around 988.1 eV assigned to ZnO on the cat-

[#1] Amounts of copper and zinc oxide at the surface of Cu/ZnO catalyst were 1.23×10^{-4} mol/g-cat and 2.20×10^{-4} mol/g-cat, respectively (surface density of copper was 1.47×10^{19} atom/m^2 [9], and that of zinc oxide was 7.29×10^{18} molecule/m^2, calculated assuming the (0001) face of zinc oxide. The BET surface area of Cu/ZnO was 18.15 m^2/g-cat, and the surface area of copper was 5.02 m^2/g-cat).

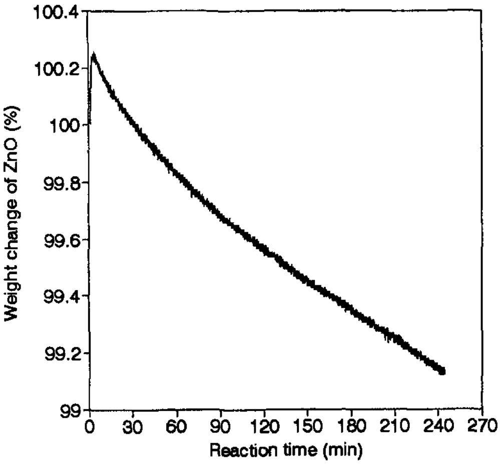

Fig. 2. Weight loss of ZnO in Cu/ZnO catalyst during the reaction with methanol at 523 K after reduction at 623 K for 1 h by 5% H_2 in Ar.

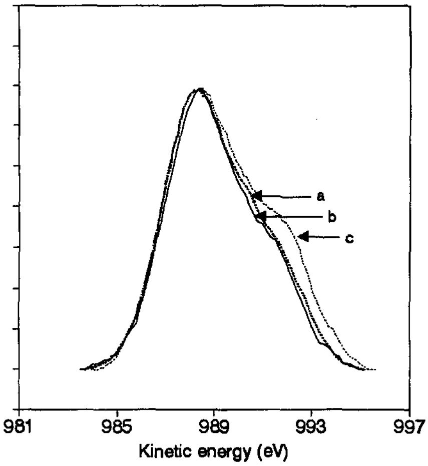

Fig. 3. Zn($L_3M_{4,5}M_{4,5}$) X-ray induced Auger spectra of Cu/ZnO catalyst: (a) calcined at 723 K for 16 h, (b) reduced at 623 K for 1 h after calcination, (c) reacted with methanol at 523 K for 3 h after calcination and reduction.

alyst surface (fig. 3). The calcined sample (a) and the reduced sample (b) show a small shoulder at 991.3 eV, which can be assigned to metallic Zn on the catalyst surface [23,24]. The shoulder at 991.3 eV (fig. 3, b) did not increase by the reduction of calcined sample (a) with hydrogen, indicating that ZnO in Cu/ZnO was not reduced by hydrogen. On the other hand, the intensity of the shoulder increased after the reaction with methanol. This increase demonstrates that ZnO in the Cu/ZnO catalyst can be reduced during the reaction with methanol. The calculation of the surface composition, using Gaussian–Lorentzian curve fitting of the Auger spectrum, gave the result that 14 mol% of ZnO on the surface of the reduced sample (fig. 3,b) was reduced to metallic zinc after the reaction with methanol at 523 K for 3 h. The shoulder of sample (c) decreased after exposing the sample to air.

The reduction of ZnO in the Cu/ZnO catalyst could be closely related to the deactivation of the catalyst. Suppression of the reduction of ZnO in the catalyst was attempted by introducing an oxidant, such as CO_2 or oxygen, into the reactant feed. Temperature-programmed reduction of the CuO/ZnO with methanol in a microbalance was performed in the presence of CO_2 with the heating rate of 10 K/min. Fig. 4 shows the weight changes of ZnO in Cu/ZnO catalyst with the various mole ratios of CO_2 to methanol. Two reduction stages in the TPR spectra were observed: (1) a sharp decrease of the weight at the lower temperature due to the reduction of copper oxide, and (2) a slow decrease of the weight at the higher temperature due to the reduction of zinc oxide. In the absence of CO_2, after the reduction of CuO in the CuO/ZnO sample over the temperature range of 450–500 K, a further 3.3% weight loss of the sample due to the reduction of ZnO was monitored, equivalent to 35 mol% reduction of ZnO in the sample. The weight loss due to reduction of ZnO was inhibited by the addition of CO_2 into the feed gas mixture.

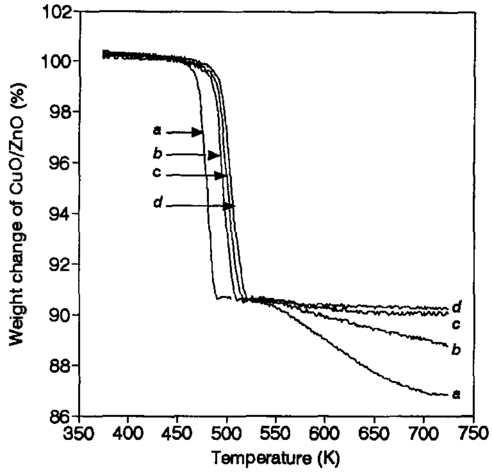

Fig. 4. TPR spectra of CuO/ZnO catalyst depending on the CO_2/methanol ratio in the helium carrier gas: heating rate 10 K/min, ratio of CO_2/methanol; (a) 0, (b) 0.3, (c) 0.6, (d) 1.0.

The weight decrease of the sample was minimized with the feed ratio of 1/1 (CO_2/methanol). The similar effect was also shown in the reduction of CuO. As the concentration of CO_2 increased, the reduction temperature of CuO was shifted from 480 K up to 500 K (fig. 4, d), The TPR experiments demonstrated that the reduction of ZnO in Cu/ZnO catalyst was suppressed in the presence of an oxidant such as CO_2.

Since the reduction of ZnO in the Cu/ZnO catalyst could be effectively controlled by CO_2, the deactivation of the catalyst for methanol dehydrogenation was studied by adding CO_2 into the feed stream. The dehydrogenation reaction was conducted under the reaction conditions: 523 K, methanol concentration of 50% in the feed stream and methanol GHSV of 3000 ml (STP/g-cat h. The mole ratios of CO_2 to methanol were 0.0, 0.3, 0.6, and 1.0 as in the TPR experiments described above. Indeed, the addition of CO_2 retarded the deactivation of Cu/ZnO catalyst (fig. 5). The conversion of methanol quickly dropped to 10% after 2 h without CO_2, while the conversion was 26% after 2 h with CO_2 (CO_2/methanol = 1/1). As the concentration of CO_2 increased, the deactivation was proportionally inhibited.

At high concentration of CO_2, the selectivity to methyl formate decreased with the formation of CO. The formation of CO might be resulted from the reverse water–gas shift reaction of CO_2 with hydrogen [25] followed by the reaction of methanol with H_2O to form CO_2 [21,22], since there was no net consumption of CO_2 during the reaction.

As shown in fig. 6, the activity of the catalyst was regenerated by the pulse injection of oxygen into the stream of methanol in helium under the reaction conditions described above. The regeneration of the activity was dependent on the amount of oxygen injected. With the injection of 2 ml oxygen into the reactor, the activity

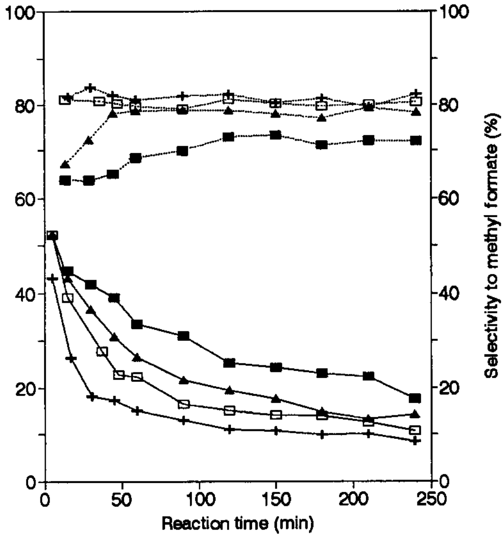

Fig. 5. Effects of the ratio of CO_2/methanol in methanol dehydrogenation at 523 K: ratio of CO_2/methanol; (+) 0, (□) 0.3, (▲) 0.6, (■) (1.0; (——) conversion of methanol, (. . .) selectivity to methyl formate.

was recovered to the initial value. The selectivities to methyl formate and CO were not affected by the oxygen injection, which suggested that the added oxygen did not react with methanol or CO, but with the catalyst. The retardation of the deactivation in the presence of an oxidant illustrated that the ZnO reduction in the Cu/ZnO catalyst could be responsible for the catalyst deactivation.

There have been many controversies on the deactivation of copper-containing

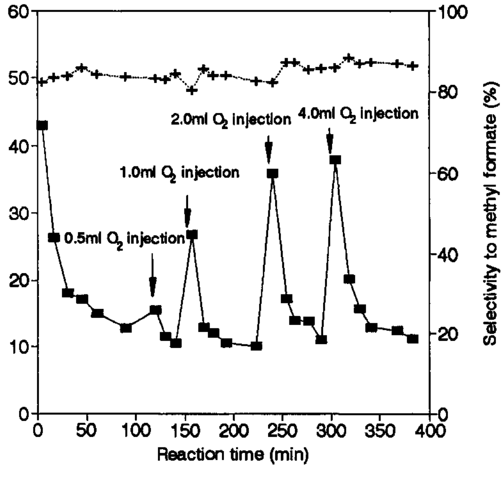

Fig. 6. Reactivation of Cu/ZnO catalyst by the injection of oxygen into the feed stream during methanol dehydrogenation at 523 K: (——) conversion of methanol, (. . .) selectivity to methyl formate.

catalysts during methanol dehydrogenation. The sintering of copper has been considered as a main reason for the deactivation. The polymerization of formaldehyde, a possible intermediate, on the surface was also proposed as a reason for the deactivation. The deactivation phenomena were dependent on the supports. Although the initial activity on methanol dehydrogenation and the selectivity to methyl formate of the Cu/ZnO catalyst were high, the deactivation of the catalyst was rather rapid. One of the important physical property changes during the deactivation of the catalyst was the weight loss due to reduction of the ZnO support. The weight loss resulting from the ZnO reduction in the catalyst was controlled and minimized effectively by the introduction of oxidizing agent such as CO_2 or oxygen. The above finding was applied to the methanol dehydrogenation. The deactivation of the catalyst was retarded by the introduction of oxidants into the feed stream. From these observations, it is concluded that the reduction of ZnO is responsible for the deactivation of Cu/ZnO catalyst in methanol dehydrogenation. It is under study how the ZnO reduction in the Cu/ZnO catalyst affects the active state of copper.

4. Conclusion

From methanol dehydrogenation on the Cu/ZnO catalyst, we have observed the following: (1) severe deactivation of Cu/ZnO catalyst and (2) reduction of the ZnO support in Cu/ZnO catalyst along with the deactivation. The reduction of ZnO in the catalyst was successfully suppressed by the addition of CO_2. Control of the reduction of ZnO in the Cu/ZnO catalyst by adding CO_2 or oxygen into the methanol feed was employed to minimize the deactivation of the catalyst. From these observations, it is concluded that the reduction of ZnO is a main reason for the deactivation of the Cu/ZnO catalyst during methanol dehydrogenation.

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