Preparation of $Cu/ZnO/M_2O_3$ (M = Al, Cr) catalyst to stabilize Cu/ZnO catalyst in methanol dehydrogenation

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ZnO reducibility in three component catalysts was monitored in a methanol stream by a microbalance. The ZnO in the Cu/ZnO is reduced in the methanol stream from *ca* 500 K, but the addition of a third component to Cu/ZnO can suppress the reduction of ZnO. The $Cu/ZnO/Cr_2O_3$ prepared from a hydrotalcite-like precursor shows high stability in methanol dehydrogenation. The high stability of $Cu/ZnO/Cr_2O_3$ is due to the stabilization of ZnO by formation of $ZnCr_2O_4$ even in the reduced condition.

KEY WORDS: methanol dehydrogenation; reduction of ZnO; solid solution; hydrotalcite precursor.

1. Introduction

Cu/ZnO-based catalysts have been used for methanol dehydrogenation to form methyl formate, the water–gas shift reaction and methanol synthesis [1]. It has been observed that the Cu/ZnO catalysts are severely deactivated in methanol dehydrogenation [2,3]. The stability of Cu/ZnO depending on the composition of the reactants has been discussed in view of the stability of Cu^{+1} [4], the sintering of copper, and the alloy formation [2,5–7]. On the other hand, Jiang *et al.* suggested that formaldehyde deposition took place on the Cu/ZnO catalyst and inhibited methanol dehydrogenation [8]. Recently, it was observed that the reduction of ZnO in the Cu/ZnO catalyst could be the main reason for the deactivation of the Cu/ZnO catalyst during methanol dehydrogenation [9]. The reduced ZnO can form α-alloy with copper in the vicinity. The sintering of copper, following the alloy formation, should be a cause of deactivation, although it can be controversial whether the α-alloy is inactive for the methanol dehydrogenation or not. Therefore, one needs to modify the Cu/ZnO catalyst to improve the stability of the catalyst. Here, Al and Cr oxides are incorporated into the Cu/ZnO catalyst to enhance the stability of the Cu/ZnO catalyst for methanol dehydrogenation. The reducibility of ZnO is correlated with the stability of the prepared catalyst.

2. Experimental

CuO/ZnO, $CuO/ZnO/Al_2O_3$ and $CuO/ZnO/Cr_2O_3$ catalysts were prepared with co-precipitating metal acetates at 298 K and pH 7. An aqueous ammonium carbonate solution (2.5 M, 400 mL) was added to the aqueous mixed metal acetate solution with an atomic ratio of the metal components of 1 : 1 or 1 : 1 : 1. The slurry was stirred at room temperature for 2 h and the precipitate was washed, filtered and dried in a vacuum oven. The dried samples were calcined at 723 K for 16 h. The prepared CuO/ZnO, $CuO/ZnO/Al_2O_3$ and $CuO/ZnO/Cr_2O_3$ catalysts will be designated to CuZn-7, CuZnAl-7 and CuZnCr-7, respectively.

The $CuO/ZnO/Al_2O_3$ and $CuO/ZnO/Cr_2O_3$ catalysts were prepared with co-precipitating metal acetate at 363 K and a pH of 9. Sodium hydroxide was used to maintain the pH of the solution at 9. The samples dried and calcined in the same way as described above were designated as CuZnAl-9 and CuZnCr-9. The atomic ratio of the metal components in the samples is 1: 1 : 1 again.

The methanol dehydrogenation reaction was conducted in a tubular reactor as previously described [9]. Methanol was introduced into the reactor by passing helium gas (120 mL/min) through the methanol saturator thermo-stated at 293 K. Reactants were analyzed with an on-line gas-chromatograph (TCD detector, Porapak Q column, $\frac{1}{8}$ in. × 10 ft). The catalyst was pre-reduced at 573 K for 3 h with 5% H_2 in Ar (60 mL/min) before the reaction. A microbalance (Cahn 2000, Cahn Instruments Inc.) was used to monitor the reduction of metal oxide with H_2 and methanol. The sample probe tube was heated with a halogen lamp heater. Samples (60 mg) were loaded on a sample pan and evacuated at 373 K to remove the remaining gases and the water on the samples in a chamber. Temperature-programmed reduction was conducted in the flow of the 5% H_2 in Ar and the methanol vapor, heating to 723 K with 10 K/min of the heating rate. For the temperature-programmed reduction with H_2, 5% H_2 in Ar (60 mL/min) was

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supplied into the sample probe. For the temperature-programmed reduction with methanol, helium gas was supplied into the sample probe through a methanol saturator (9.2% methanol in helium, 120 mL/min) after the catalyst was pre-reduced at 573 K for 3 h with 5% H_2 in Ar (60 mL/min) before the reduction with methanol.

X-ray powder diffractograms (Rigaku D-Max-IIIA diffractometer) were recorded using Cu K_α targets to examine the structure of the oxide samples. The reduced samples were prepared in a glove box and sealed with Midac film.

3. Results and discussion

Figure 1 shows the methanol conversion and the selectivity of methanol to methyl formate at 523 K and 3000 mL/g_{cat} h of GHSV with the Cu/Zn-7, CuZnAl-7 and CuZnCr-7 catalysts. The activity of the CuZnCr-7 catalyst is the highest among the three catalysts at 15 min, while that of the CuZn-7 catalyst is the lowest. The low activity of the Cu/ZnO can be due to the severe deactivation during the reaction. The distinctive feature of the catalysts obtained by adding oxides such as Al_2O_3 and Cr_2O_3 to the Cu/ZnO is to stabilize the Cu/ZnO. Nonetheless, the conversion of methanol slightly decreases on the CuZnAl-7 and CuZnCr-7 catalysts during the reaction. The selectivity of methanol to methyl formate is the highest on the Cu/ZnO within 30 min, but on the CuZnAl-7 afterwards. The Cu/ZnAl-7 catalyst can effectively suppress the deactivation of the Cu/ZnO without changing the selectivity of methanol to methyl formate, different from the CuZnCr-7 catalyst. The main by-product of methanol dehydrogenation is carbon monoxide. It was reported that the CO cannot come from the shift reaction but from the decomposition of methyl formate into methanol and CO [8]. This means that methyl formate can be decomposed better on the CuZnCr-7 catalyst than on the CuZn-7 and CuZnAl-7 catalysts.

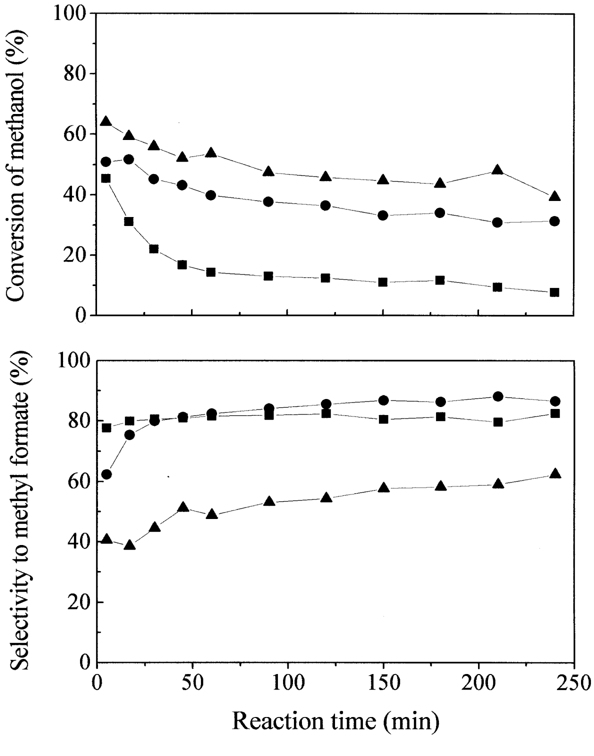

Figure 1. Methanol dehydrogenation on CuZn-7 (■), CuZnAl-7 (●) and CuZnCr-7 (▲) (GHSV = 3000 mL (MeOH)/g_{cat} h, reaction temperature = 523 K).

It was already shown that the deactivation of the CuZn-7 catalyst was due to the reduction of ZnO during the methanol dehydrogenation [9]. From this point of view, the enhancement of the stability of the CuZnAl-7 and CuZnCr-7 can be due to the suppression of the reduction of ZnO. To investigate the reducibility of ZnO in CuZnAl-7 and CuZnCr-7, temperature-programmed reductions were conducted in a methanol stream in a microbalance.

Before the investigation of the reducibility of ZnO, the reduction behaviors of CuO in the CuZn-7, CuZnAl-7 and CuZnCr-7 catalysts should be studied in a stream of 5% H_2 in Ar. Figure 2 shows the temperature-programmed reduction in an H_2 flow with the CuZn-7, CuZnAl-7 and CuZnCr-7. The weight loss based on CuO indicates the total weight loss divided by the weight of CuO in the catalysts. The copper oxides in the CuZn-7, CuZnAl-7 and CuZnCr-7 are reduced at 470, 495 and 560 K, respectively. The CuO in the CuZnCr-7 is reduced in a broad temperature range from 450 to 650 K. Joo *et al.* suggested that the high-temperature reduction (500 K) of CuO in the Cu/ZnO/Al_2O_3 (3 : 6 : 1) catalyst indicated the presence of copper ion in the solid solution [10]. The CuO in the CuZnAl-7 in this study is

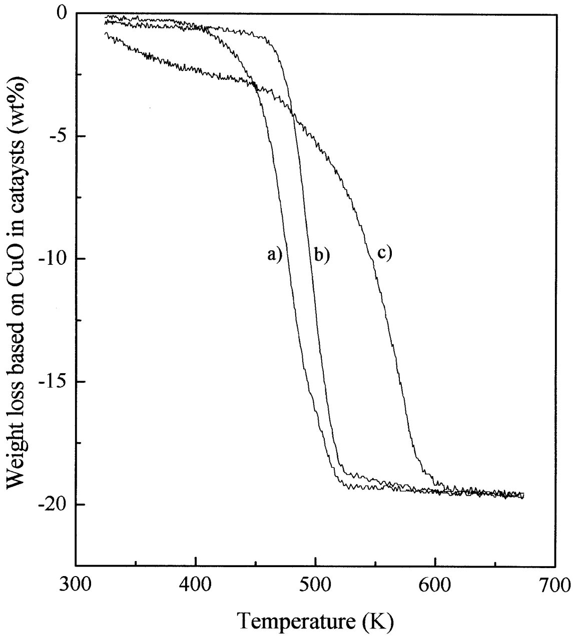

Figure 2. Temperature-programmed reduction of CuO in (a) CuZn-7, (b) CuZnAl-7 and (c) CuZnCr-7, with 5% H_2 in Ar (60 mL/min).

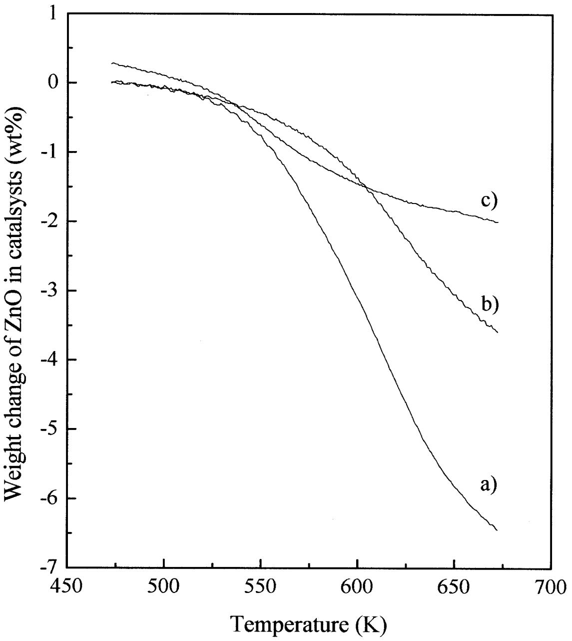

Figure 3. Temperature programmed reduction of ZnO in (a) CuZn-7, (b) CuZnAl-7 and (c) CuZnCr-7 in a stream of methanol, after reducing the copper component to metallic copper at 573 K for 3 h with 5% H_2/Ar (60 mL/min).

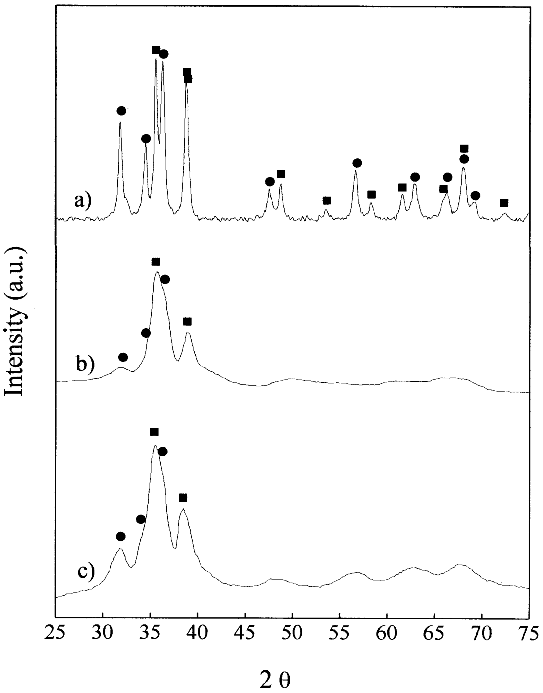

Figure 4. X-ray diffractograms of (a) CuZn-7, (b) CuZnAl-7 and (c) Cu/ZnCr-7 oxides: ZnO (●), CuO (■).

reduced at 60 K higher temperature than the one in the Cu/ZnO/Al_2O_3 (3 : 6 : 1) catalyst. The high reduction temperature of CuO in the CuZnAl-7 can be attributed to the high interaction between CuO and Al_2O_3 oxides.

To investigate the ZnO reducibility in the CuZn-7, CuZnAl-7 and CuZnCr-7 catalyst, temperature-programmed reduction was conducted from 473 to 673 K in a stream of methanol after CuO in the catalysts was reduced to elementary copper metal in 5% H_2 in Ar (60 mL/min) at 573 K for 3 h. The weight loss based on ZnO means the total weight loss of the sample divided by the weight of ZnO in the catalyst sample. Figure 3 shows the reduction behavior of ZnO in a methanol stream. ZnO in the CuZn-7 is severely reduced in the temperature range from 473 to 673 K, while that in the CuZnAl-7 is slightly reduced up to 600 K and sharply reduced after 600 K. The reduction of ZnO in the CuZnCr-7 can be effectively suppressed up to 723 K. The reducibility of the ZnO reduction in the three catalysts is well correlated with the deactivation of the Cu/ZnO-based catalysts; supporting the reduction of ZnO can be the cause of the deactivation for methanol dehydrogenation [9].

Figure 4 shows the X-ray diffractograms of the CuZn-7, CuZnAl-7 and CuZnCr-7 oxides. The X-ray diffractogram of the CuZn-7 shows the characteristic peaks of ZnO ($2\theta = 36$, 34, 32°) and CuO ($2\theta = 39$, 35, 48°), while the X-ray diffractograms of the CuZnAl-7 and CuZnCr-7 samples show broad peaks at the characteristic positions of ZnO and CuO. This indicates that the ZnO and CuO particles are finely dispersed in the Al_2O_3 and Cr_2O_3 matrix, although a spinel structure formation such as $ZnAl_2O_3$ or $ZnCr_2O_4$ cannot be ruled out.

It has been reported that the most active methanol synthesis catalysts are based on an intimate mixture of Cu/ZnO prepared by calcinations of the co-precipitated precursor obtained at 293 K and a pH of 7 [1]. From the above experimental results, the catalysts prepared by the usual method were severely deactivated in methanol dehydrogenation, although the addition of a third component to the CuO/ZnO catalyst could enhance the stability and the activity. It is well known that the catalyst structures are dependent on the preparation conditions, such as the pH of the solution and the temperature of the solution. The precursors of the hydrotalcite-like structure can be prepared at 363 K and a pH of 9. Figures 5 and 6 show the X-ray diffractograms of the dried precursors and the calcined samples, prepared at 363 K and a pH of 9, respectively.

The characteristic peaks of the CuZnAl-9 precursor coincide with the reference spectrum of the hydrotalcite [11,12]. The absence of the peak at $2\theta = 35.5°$ in the CuZnAl-9 indicates that the hydrotalcite-like precursor has a stacking sequence of the rhombohedral structure only [12]. The precursors of the CuZnCr-9 show broad peaks around $2\theta = 12.5$, 22.5, 35 and 60°, which are the characteristic peaks of the hydrotalcite-like structure [12]. The oxide catalysts from the hydrotalcite precursors show a spinel structure. The CuZnAl-9 has a broad peak at $2\theta = 32°$ and the CuZnCr-9 has broad peaks at $2\theta = 30$, 35, 43, 54, 57 and 63°.

Figure 7 shows the conversion and selectivity for methanol dehydrogenation at 493K and GHSV of 3000 mL (methanol)/g_{cat} h on the CuZnAl-9 and

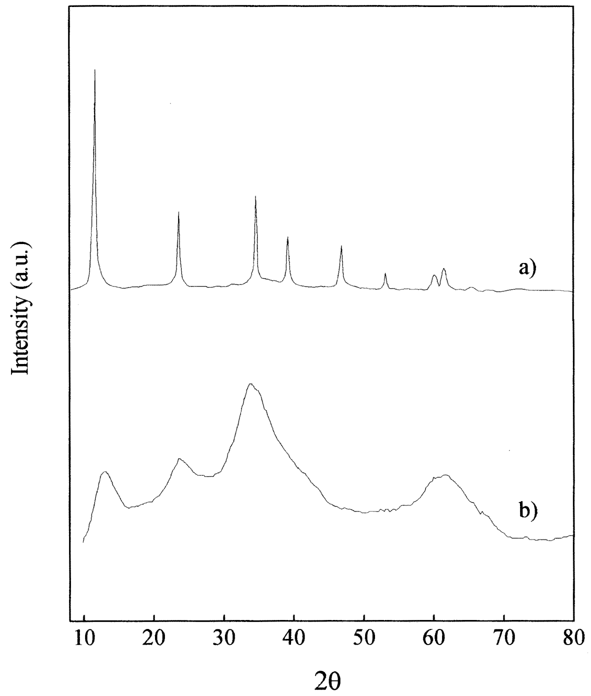

Figure 5. X-ray diffractograms of the precursors of (a) CuZnAl-9 and (b) CuZnCr-9 oxides.

CuZnCr-9 catalysts. The CuZnCr-9 catalyst shows high stability and activity, different from the CuZnCr-7 catalyst. The methanol conversion rather increases from 46% at 15 min to 50% at 4 h on the CuZnCr-9. The CuZnAl-9 catalyst shows a similar stability and activity to the CuZnAl-7. It is interesting to note that the CuZnAl-9 and CuZnCr-9 show a different behavior on the stability for methanol dehydrogenation, although both catalysts have the same spinel structure.

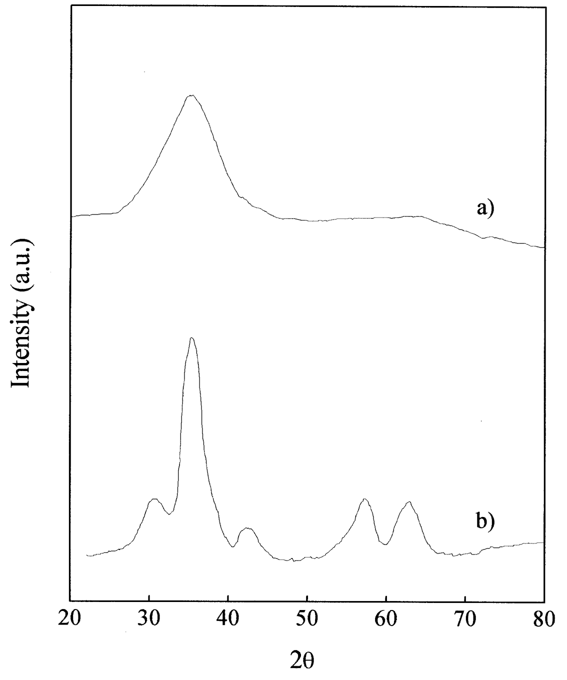

Figure 6. X-ray diffractograms of (a) CuZnAl-9 and (b) CuZnCr-9 oxides.

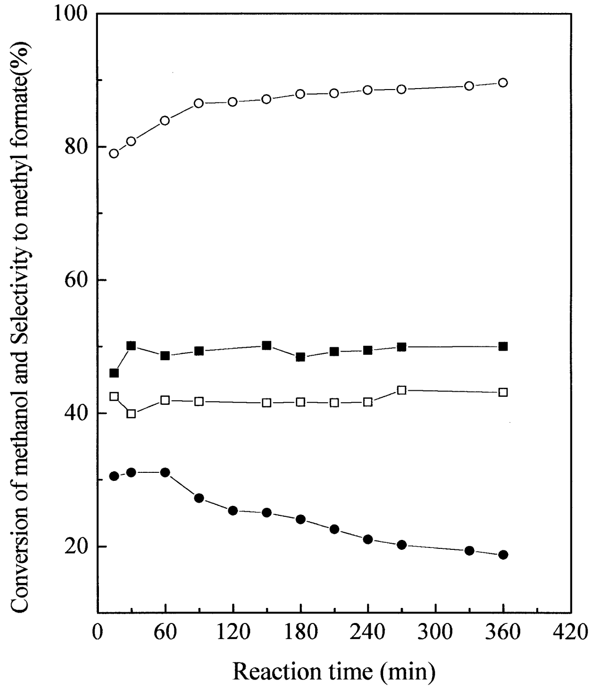

Figure 7. Methanol dehydrogenation on the catalysts prepared from a hydrotalcite-like precursor (3000 mL(MeOH)/g_{cat} h, reaction temperature = 523 K): conversion of methanol (●) and selectivity of methanol to methyl formate (○) on CuZnAl-9; conversion of methanol (■) and selectivity of methanol to methyl formate (□) on CuZnCr-9.

To investigate the structural differences between the CuZnAl-9 and CuZnCr-9 samples, X-ray diffractograms of CuZnAl-9 and CuZnCr-9 reduced with H_2 are obtained, as shown in figure 8. Both catalysts are reduced at 723 K for 3 h in a stream of 5% H_2 in Ar. The Cu metal

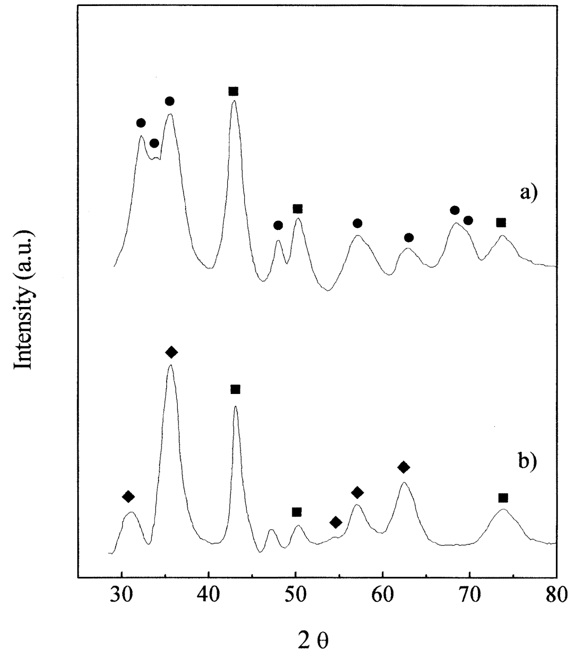

Figure 8. X-ray diffractograms of (a) CuZnAl-9 and (b) CuZnCr-9 catalysts, reduced at 573 K for 3 h with 5% H_2/Ar (60 mL/min): ZnO (■), Cu metal (●), $ZnCr_2O_4$ (◆).

($2\theta = 43, 50, 74°$) and ZnO ($2\theta = 36, 34, 32°$) characteristic peaks appear in the reduced CuZnAl-9 sample, while the ZnO peaks are not shown in the reduced CuZnCr-9 catalyst. The reduced CuZnCr-9 catalyst shows the Cu metal peaks and the $ZnCr_2O_4$ peaks ($2\theta = 36, 63, 57, 54, 44°$).

It indicates that ZnO can be stabilized in the form of $ZnCr_2O_4$ spinel [13] on the CuZnCr-9 catalyst, even in the reductive condition. Therefore, the reduction of ZnO can be prevented even in a methanol stream. As previously described, the deactivation of the Cu/ZnO-based catalysts is due to the reduction of ZnO in the vicinity of Cu metal. It can be concluded that the prevention of the ZnO reduction by the $ZnCr_2O_4$ spinel formation can give high stability to the CuZnCr-9 catalyst in methanol dehydrogenation.

4. Conclusions

The stability of the CuZn-7, CuZnAl-7 and CuZnCr-7 in methanol dehydrogenation is correlated with the reduction of ZnO in a methanol stream. The CuZnCr-9 catalyst prepared from hydrotalcite-like precursors shows a high stability and activity for methanol dehydrogenation. The high stability of the CuZnCr-9 catalyst results from the prevention of the ZnO reduction by the $ZnCr_2O_4$ spinel formation.

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