

Stability of ZnAl₂O₄ Catalyst for Reverse-Water-Gas-Shift Reaction (RWGSR)

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Reverse-Water-Gas-Shift reaction (RWGSR) was carried out over the ZnO, Al₂O₃, and ZnO/Al₂O₃ catalysts at the temperature range from 400 to 700 °C. The ZnO showed good specific reaction activity but this catalyst was deactivated. All the catalysts except the ZnO/Al₂O₃ catalyst (850 °C) showed low stability for the RWGSR and was deactivated at the reaction temperature of 600 °C. The ZnO/Al₂O₃ catalyst calcined at 850 °C was stable during 210 hrs under the reaction conditions of 600 °C and 150,000 GHSV, showing CO selectivity of 100% even at the pressure of 5 atm. The high stability of the ZnO/Al₂O₃ catalyst (850 °C) was attributed to the prevention of ZnO reduction by the formation of ZnAl₂O₄ spinel structure. The spinel structure of ZnAl₂O₄ phase in the ZnO/Al₂O₃ catalyst calcined at 850 °C was confirmed by XRD and electron diffraction.

Key Words : RWGSR, Reducibility, Stability, Spinel

Introduction

The conversion of CO₂ into chemical resources has been attempted by several methods to mitigate the greenhouse effects.¹⁻⁴ Especially, the catalytic hydrogenation of CO₂ to form methanol is one of the efficient processes being able to treat a large quantity of CO₂ and the produced methanol can be consumed in the conventional chemical industry. We have reported CAMERE (Carbon Dioxide Hydrogenation to Form Methanol via a Reverse-Water-Gas-Shift Reaction) process to convert CO₂ into methanol, which consists of a reverse-water-gas-shift reaction (RWGSR) and a methanol synthesis reaction.⁵ In this report, carbon dioxide and hydrogen were converted to CO and H₂O by RWGSR and then, the mixture gas of CO/CO₂/H₂ was fed into the methanol synthesis reactor after removing the water. Methanol yield become high if the conversion of CO₂ to CO in the RWGSR is high because the CO can react with water on the methanol synthesis catalyst, chemically removing the water on the catalyst and forwardly driving methanol synthesis reaction. Therefore, the development of an active and stable catalyst for the RWGSR was important for the CAMERE process.

The water-gas-shift reaction has been intensively studied for the last several decades for H₂ production from synthesis gas. On the contrary, a reverse-water-gas-shift reaction has attracted little attention because of little demand. The Fe₂O₃/Cr₂O₃ catalyst is a well-known commercial catalyst for the water-gas-shift reaction.⁶ The commercial catalyst, Fe₂O₃/Cr₂O₃, was a logical candidate for the RWGSR of the CAMERE process. But, the Fe₂O₃/Cr₂O₃ catalyst was easily reduced into the iron metal under high reaction temperature for the RWGSR,⁷ clogging the reactor with carbon formation on the metal.

In this paper, we reported the activities of the ZnO, Al₂O₃,

and ZnO/Al₂O₃ (Zn : Al = 1 : 2) catalysts examined for the RWGSR. The ZnO showed the highest specific activity but the catalyst was easily deactivated. It was found that ZnAl₂O₄ phase only showed good stability at the high reaction temperature for the RWGSR.

Experimental Section

ZnO, Al₂O₃, and ZnO/Al₂O₃ (Zn : Al = 1 : 2) catalysts were prepared by a co-precipitation of the corresponding metal nitrates (Zn(NO₃)₂, Al(NO₃)₃; Kanto Chemical Co., Inc.) at pH 7.⁸ The catalysts were calcined at 500 or 850 °C for 3 hr, which were described in the form of catalysts (500 or 850 °C). The activities of the catalysts were studied for the RWGSR at the temperature range of 400-700 °C with GHSV (mL/g_{cat}.h) of 15,000. The stability of the ZnO and ZnO/Al₂O₃ catalysts (850 °C) was evaluated under the severe reaction conditions of 600 and 700 °C and GHSV of 150,000. The catalyst charged in a tubular reactor was heated up to the reaction temperature in the presence of CO₂ and H₂ before the RWGSR. The RWGSR was carried out at atmosphere pressure with the H₂/CO₂ ratio of 3 in the reactant gas. The exit gas was monitored with a gas chromatograph (Shimadzu 8A instrument with a TCD, Porapak Q column 1/8" o.d., 3 m long in program temperature mode for analysis of CO, CO₂, H₂, CH₄ and H₂O).

The BET surface areas of the catalysts were measured by ASAP 2000 (Micromeritics). The bulk structure of the ZnO, Al₂O₃, and ZnO/Al₂O₃ catalysts was examined using a XRD and an electron microscopy. The X-ray powder diffraction patterns were recorded by a Rigaku D-Max-III A diffractometer with CuK α radiation. TEM & E.D. (200 kV) images of the used catalysts were obtained by a Phillips CM-30 scanning transmission electron microscopy. The specimen was prepared by making the suspension of a catalyst sample and then, dipping a carbon grid with holes into the suspension and drying the carbon grid. TPR (Temperature Programmed Reduction) experimental was conducted in a

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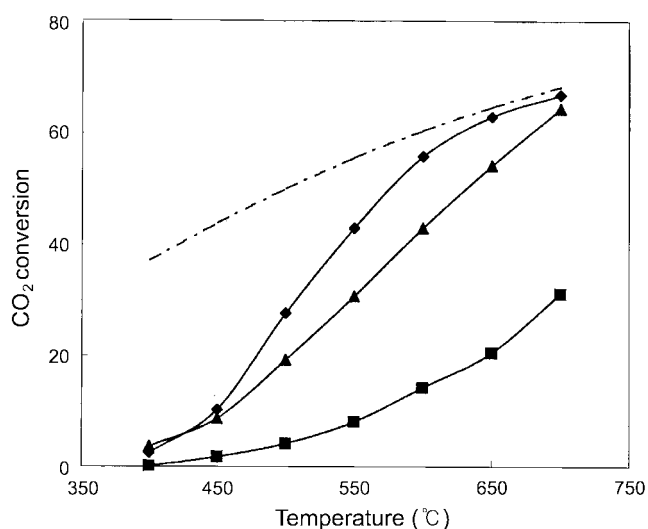


Figure 1. CO₂ conversion on the ZnO, ZnO/Al₂O₃, and Al₂O₃ catalysts (500 °C). GHSV=15,000. ---: Equil, ♦: ZnO, ■: Al₂O₃, ▲: ZnO/Al₂O₃.

tubular reactor in a stream of 5% H₂/Ar with 20 °C/min of a ramping rate. The amount of H₂ consumption was monitored using a TCD.

Results and Discussion

The activities of the ZnO, Al₂O₃, and ZnO/Al₂O₃ catalysts were tested for the reverse-water-gas-shift reaction (RWGSR). Figure 1 showed the activities for the catalysts (500 °C). The ZnO (500 °C) showed nearly equilibrium conversion at 650 °C and the conversion of the ZnO/Al₂O₃ catalyst (500 °C) approached to the equilibrium above 700 °C. The Al₂O₃ showed the lowest activity among the three catalysts for the RWGSR, which was about one third of ZnO. Methane (by-product) was not detected in the reaction.

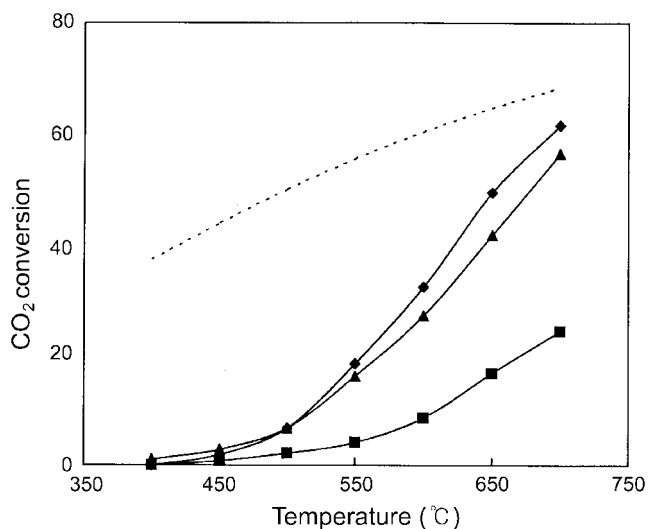


Figure 2. CO₂ conversion on the ZnO, ZnO/Al₂O₃, and Al₂O₃ catalysts (850 °C). GHSV=15,000. ---: Equil, ♦: ZnO, ■: Al₂O₃, ▲: ZnO/Al₂O₃.

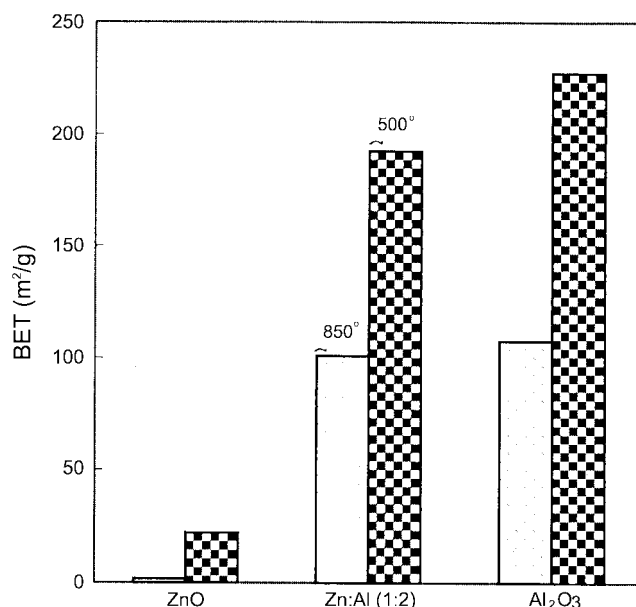


Figure 3. BET surface area of ZnO, ZnO/Al₂O₃, and Al₂O₃ catalysts depending on the calcination temperature.

Figure 2 indicated the activities for the catalysts (850 °C). Figure 3 showed the BET surface area of the catalysts depending on the calcination temperature. The calcination at 850 °C decreased the BET surface area and also the activities for the RWGSR. The surface area of the ZnO/Al₂O₃ catalysts (500 or 850 °C) was a little smaller than those of Al₂O₃ (500 or 850 °C) but the activities were much higher than those of the Al₂O₃. The activity of the ZnO/Al₂O₃ catalysts (850 °C) decreased into the 41.7% CO₂ conversion from the 54% conversion on the ZnO/Al₂O₃ catalyst (500 °C) at the reaction temperature of 650 °C. With calcination at 850 °C, the activity of the Zn/Al₂O₃ catalyst decreased about 12% at the reaction temperature of 650 °C, whereas the BET surface area of the ZnO/Al₂O₃ catalyst decreased from 192.5 to 108.0 m²/g_{cat}. The ZnO gave good specific activity as compared with the ZnO/Al₂O₃ and the Al₂O₃ catalysts. The CO₂ conversion of 62.7% on the ZnO (500 °C) decreased into the 49.4% on the ZnO (850 °C) at the reaction temperature of 650 °C. On the other hand, the BET surface area of the ZnO catalyst decreased from 22.0 to 1.5 m²/g_{cat}. However, it is interesting to mention that the ZnO catalyst (850 °C) showed the high specific activity.

The CAMERE process consists of a reverse-water-gas-shift reaction (RWGSR) and a methanol synthesis reaction.⁵ The conversion of CO₂ into CO in the reverse-water-gas-shift reactor should be increased as high as possible. Then, the feed gas with high CO concentration from the reverse water-gas-shift reactor into the methanol synthesis reactor could result in the high methanol yield. The conventional active oxide catalysts for the RWGSR were mostly reduced at the high temperature above 400 °C and then, deactivated.⁷ Therefore, the stable catalysts even with a little bit lower activity should be important for the RWGSR in the CAMERE process. Although the ZnO catalyst showed good specific activities for the RWGSR, the ZnO (500 or 850 °C)

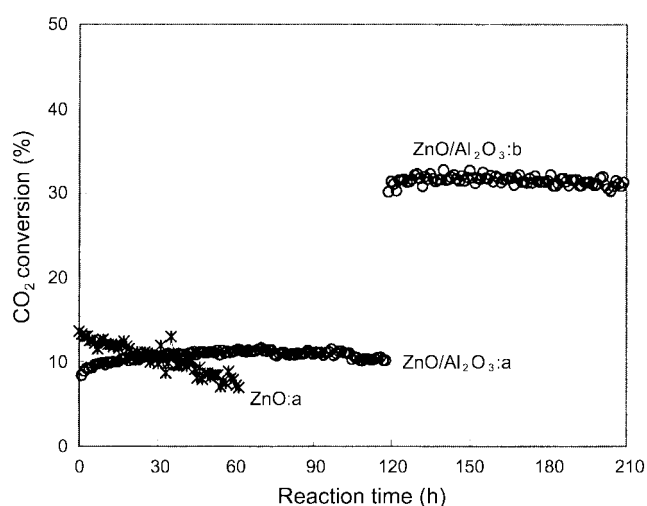


Figure 4. CO₂ conversion on the ZnO and ZnO/Al₂O₃ catalysts (850 °C) with the reaction time at the GHSV of 150,000. a: reaction temp. of 873 K, b: reaction temp. of 973 K.

was reduced from 500 to 1000 °C depending on the calcination temperature,^{9,10} causing the catalyst deactivation. The ZnO/Al₂O₃ catalyst (500 °C) was also deactivated with reaction time at reaction temperature of 600 °C. The life test was performed on the ZnO and ZnO/Al₂O₃ catalysts (850 °C) at GHSV of 150,000 and 600 °C and then, 700 °C to confirm the stability in a short time as shown in the Figure 4. The ZnO (850 °C) was gradually deactivated with reaction time. Only ZnO/Al₂O₃ catalyst (850 °C) did not deactivate at the reaction temperature of 600 and 700 °C. A catalyst life for a day with GHSV of 150,000 meant that the catalyst would be operated for 50 days in the real system operated at the GHSV of 3,000. Therefore, the ZnO/Al₂O₃ catalyst (850 °C) would be durable more than one year in the reaction conditions of the CAMERE process. The conventional oxide catalysts for the RWGSR were reduced at high reaction temperature above 400 °C and then, by-product of methane made even at atmosphere pressure.^{6,7} But, the methane was not produced on the ZnO/Al₂O₃ catalyst (850 °C) even at 5atm because the catalyst was not reduced into the metal. The ZnO/Al₂O₃ catalyst (850 °C) did not deactivate for the reaction time of 210 hrs even at 700 °C as shown in the Figure 4.

The structure of the ZnO, Al₂O₃, and ZnO/Al₂O₃ catalysts (850 °C) was monitored by XRD. The XRD patterns were shown in the Figure 5. The Al₂O₃ (500 °C) did not show any crystalline structure but the Al₂O₃ (850 °C) show a little crystalline structure like in the spectrum in the Figure 5. On the other hand, the ZnO and ZnO/Al₂O₃ catalysts (850 °C) showed good crystalline structure. Figure 5 showed that the ZnO/Al₂O₃ catalyst (850 °C) was the spinel structure of ZnAl₂O₄, which was monitored by the XRD.

Figure 6 indicated the TEM images and the electron diffraction pattern of the ZnO and ZnO/Al₂O₃ catalysts depending on the calcination temperature of 500 or 850 °C. TEM images showed that the particle size of the ZnO (500 °C) about 100 nm was sintered into the larger particle than

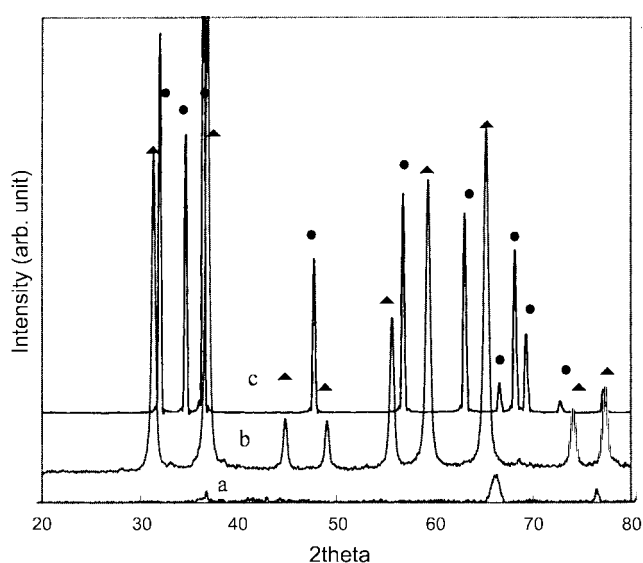


Figure 5. XRD spectra of the Al₂O₃, ZnO/Al₂O₃, and ZnO catalysts (850 °C). a: Al₂O₃, b: ZnO/Al₂O₃, c: ZnO; ▲ : ZnAl₂O₄, ● : ZnO.

500 nm by the heat treatment at 850 °C. The scattered spots of the ZnO (500 °C) were shown by the electron diffraction for the selected area including a few number of ZnO (500 °C) particles. The approximate *d* values could be calculated from the radius of the electron diffraction for the ZnO (500 °C) as shown in Table 1, although the ring pattern was not so clear due to a small number of particles. The interplanar spacings *d* values were calculated by the basic equation $d = \lambda L/R$ from the distance *R* of the diffraction spot from the origin.¹¹ Where, λ was 0.02508 Å at 200 kV, *L* was 300 mm. The calculated *d* values were coincided with the *d* values of the crystalline structure of the ZnO. The electron diffraction for a particle of the ZnO (850 °C) was obtained. The spots indicated that the ZnO (850 °C) was a single crystal. The electron diffraction pattern for the ZnO (850 °C) was for an [101] axis. It was confirmed from the angle between the reciprocal lattice points (101) and (010), and the *d* values of (101) and (010) plane. The TEM image of the ZnO/Al₂O₃ catalyst (500 °C) was shown in (c) of the figure 6 and the ZnO/Al₂O₃ catalyst (500 °C) did not make a uniform phase. Two phases of ZnO and ZnAl₂O₄ were confirmed from the *d* values of the radius of the electron diffraction pattern. The ZnAl₂O₄ phase in the ZnO/Al₂O₃ catalyst (500 °C) was also confirmed by the XRD but the intensity was not strong as compared with that in the ZnO/Al₂O₃ catalyst (850 °C). Moreover, the excess Al₂O₃ phase in the ZnO/Al₂O₃ catalyst (500 °C) could not be discriminated from the ZnAl₂O₄ phase by the XRD. The TEM image and the electron diffraction pattern of the ZnO/Al₂O₃ catalyst (850 °C) were shown in (d) of the Figure 6.

The TEM image indicated that the ZnO/Al₂O₃ catalyst (850 °C) made a uniform phase. The calculated *d* values from the radius of the electron diffraction pattern for the ZnO/Al₂O₃ catalyst (850 °C) were coincided with the *d* values of the ZnAl₂O₄ crystalline structure. The electron diffraction pattern for the ZnO/Al₂O₃ catalyst (850 °C)

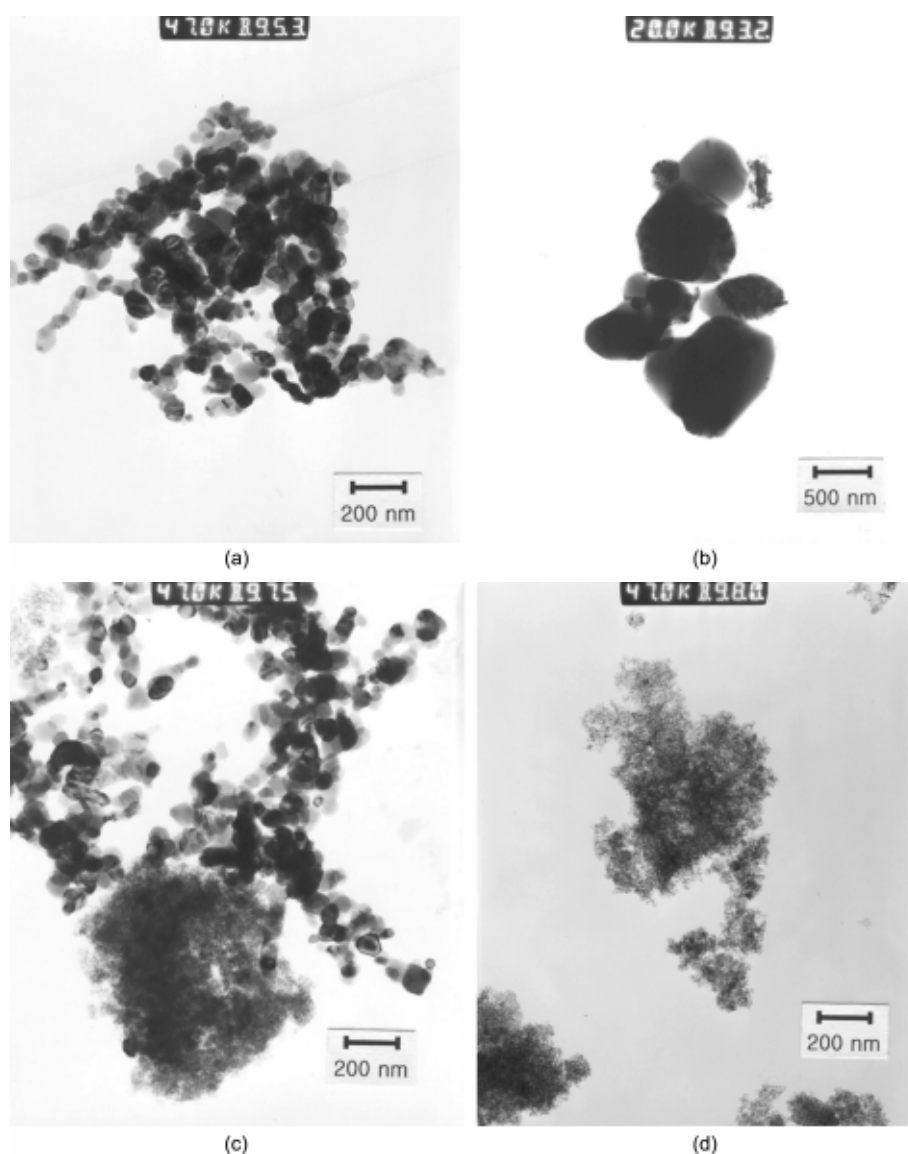


Figure 6. TEM images and electron diffraction patterns of the ZnO and ZnO/Al₂O₃ catalysts depending on the calcination temperature. a: ZnO (500 °C), b: ZnO (850 °C), c: ZnO/Al₂O₃ (500 °C), d: ZnO/Al₂O₃ (850 °C)

Table 1. Comparison the *d* values of ZnO and ZnAl₂O₄ crystalline structure with the calculated *d* values from the radius of the electron diffraction pattern

ZnO		ZnAl ₂ O ₄	
<i>d</i> values	Calculated <i>d</i> values	<i>d</i> values	Calculated <i>d</i> values
2.814 (57)	2.894	2.861 (84)	2.894
2.603 (44)	2.594	2.438 (100)	2.427
2.476 (100)	2.508	1.855 (10)	1.980
1.911 (23)	1.929	1.650 (24)	1.635
1.6247 (32)	1.635	1.556 (40)	1.472
		1.429 (43)	1.419

showed the distinct ring pattern, which meant the ZnO/Al₂O₃ catalyst (850 °C) had good crystalline structure. The calculated *d* values of ZnO/Al₂O₃ were compared with the *d* values of the ZnAl₂O₄ crystalline structure in the Table 1.

The ZnO/Al₂O₃ catalyst (500 °C) showed good activity than the Zn/Al₂O₄ catalyst (850 °C) as shown in the Figure 1 and 2. But, the ZnO/Al₂O₃ catalyst (500 °C) lost the activity with the reaction time at the temperature of 600 °C because most ZnO in the ZnO/Al₂O₃ catalyst (500 °C) did not form the ZnAl₂O₄ phase and the ZnO and ZnAl₂O₄ phase were separated in the ZnO/Al₂O₃ catalyst. Only ZnAl₂O₄ phase was stable for the RWGSR and the spinel structure of ZnAl₂O₄ in the ZnO/Al₂O₃ catalyst (850 °C) was confirmed by XRD and electron diffraction. As previously suggested, the high stability of ZnAl₂O₄ for the RWGSR could be related to the reducibility of the catalyst sample. TPR (temperature programmed reduction) in 5%H₂/Ar was conducted to investigate the reducibility of ZnO (850 °C) and Zn/Al₂O₄ (850 °C). The ZnO (850 °C) started to be reduced at 750 °C, while the Zn/Al₂O₄ (850 °C) was not reduced up to 1100 °C. Therefore, the stability of the Zn/Al₂O₄ (850 °C) was enhanced by the formation of the

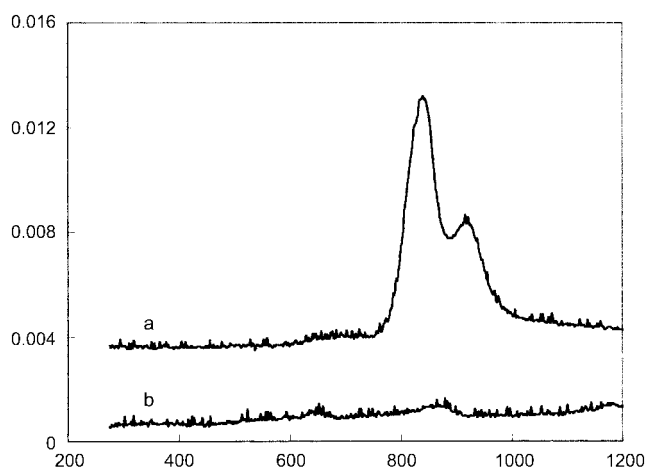


Figure 7. Temperature programmed reduction of ZnO and ZnO/Al₂O₃ (850 °C) in a stream of 5 %H₂/Ar. a: ZnO (850 °C), b: ZnO/Al₂O₃ (850 °C).

ZnAl₂O₄ spinel structure as compared with that of the ZnO, while the activity of the Zn/Al₂O₄ (850 °C) was increased by the ZnO component as compared with that of the Al₂O₃.

Conclusions

The ZnO/Al₂O₃ catalyst (850 °C) was made of the spinel structure of ZnAl₂O₄, which was confirmed by XRD and electron diffraction. The ZnAl₂O₄ catalyst was stable till 210 hrs under 600 and 700 °C and GHSV of 150,000, although

the activity was less than those of the ZnO and the ZnO/Al₂O₃ catalysts (500 °C). Whereas, the ZnO (850 °C) was gradually deactivated with the reaction time, even though the catalyst had the high specific activity for the RWGSR.

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