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ZnO/Cr_2O_3 Catalyst for Reverse-Water-Gas-Shift Reaction of CAMERE Process

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Abstract−The stability and the activity of Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 catalysts were examined for a reverse-water-gas-shift reaction (RWReaction). The initial activities of those catalysts were quite high so that the conversion reached close to equilibrium. The activity of Fe_2O_3/Cr_2O_3 catalyst decreased from 33.5 to 29.8% during the RWReaction for 75 h at 873 K with GHSV ($ml/g_{cat}\cdot h$) of 100,000. Moreover, the coke formation on the Fe_2O_3/Cr_2O_3 catalyst caused clogging in the RWReactor of the CAMERE process. On the other hand, the ZnO/Cr_2O_3 catalyst showed no coke formation and no deactivation for the RWReaction at 873 K with GHSV ($ml/g_{cat}\cdot h$) of 150,000. The ZnO/Cr_2O_3 was a good catalyst for the RWReaction of the CAMERE process.

Key words: CAMERE Process, Reverse-Water-Gas-Shift Reaction, Fe_2O_3/Cr_2O_3, ZnO/Cr_2O_3

INTRODUCTION

The conversion of CO_2 to chemical resources has been attempted by several methods to mitigate greenhouse effects [Jessop et al., 1995; Usui and Ikenouchi, 1997; Kitamura and Tazuke, 1983; Lee et al., 1999]. In particular, the catalytic hydrogenation of CO_2 to form methanol [Shen et al., 2000] is an efficient process for treating a large quantity of CO_2, minimizing the hydrogen loss compared with that of hydrocarbon production.

We have reported the CAMERE (Carbon Dioxide Hydrogenation to Form Methanol via a Reverse-Water-Gas-Shift Reaction) process to convert CO_2 into methanol, which consists of a reverse-water-gas-shift reaction (RWReaction) and a methanol synthesis reaction [Joo et al., 1999]. In the CAMERE process, carbon dioxide and hydrogen were converted to CO and H_2O by RWReaction, and then the mixture gas of $CO/CO_2/H_2$ was fed into the methanol synthesis reactor after water was removed. The higher the conversion of CO_2 to CO was in the RWReaction, the higher the methanol productivity was in the CAMERE process [Park et al., 2000]. Therefore, the development of an active and stable catalyst for the RWReaction was a critical requirement for the CAMERE process.

For several decades the water-gas-shift reaction has been studied intensively in order to adjust the H_2/CO ratio in the synthesis gas. However, because of limited demand, the reverse-water-gas-shift reaction has attracted little attention. The Fe_2O_3/Cr_2O_3 catalyst is a well-known commercial catalyst for the water-gas-shift reaction [Twigg, 1989]. The commercial catalyst Fe_2O_3/Cr_2O_3 was a logical candidate for the RWReaction of the CAMERE process. In this report the activity and the stability of the Fe_2O_3/Cr_2O_3 catalyst were investigated for the RWReaction. The Fe_2O_3/Cr_2O_3 catalyst showed severe deactivation, which was attributed to the reduction of Fe_2O_3 to the Fe metal. As a result, a new type of catalyst for the RWReaction, ZnO/Cr_2O_3, was developed. The ZnO/Cr_2O_3 catalyst showed good activity and stability without coke formation.

EXPERIMENTAL

The ZnO/Cr_2O_3 catalyst (Zn : Cr=2 : 1 in molar ratio) was prepared by a co-precipitation of the corresponding metal nitrates [Joo et al., 1996]. The catalyst was calcined at 773 K before the RWReaction. The activities of the ZnO/Cr_2O_3 and a Fe_2O_3/Cr_2O_3 (Fe : Cr= 9 : 1 in molar ratio) catalysts were studied for the RWReaction at the temperature range of 673-1,023 K with GHSV ($ml/g_{cat}\cdot h$) of 15,000. The RWReaction was carried out at atmosphere pressure with an H_2/CO_2 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, CO_2, H_2, CH_4 and H_2O).

The BET surface areas of the catalysts were measured by ASAP 2000 (Micromeritics), and they were 82.1 m^2/g for the ZnO/Cr_2O_3 and 70.4 m^2/g for the Fe_2O_3/Cr_2O_3. Also, the stability of the catalysts was tested under severe reaction conditions of 873 K and GHSV of 100,000 (Fe_2O_3/Cr_2O_3) and 150,000 (ZnO/Cr_2O_3). The catalyst charged in a tubular reactor was heated to the reaction temperature in the presence of CO_2 and H_2 before the RWReaction. The catalysts were characterized by using Temperature-Programmed Oxidation (TPO) and XRD. TPO was performed to confirm the coke formed on the surfaces of Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 after the RWReaction. TPO was performed at a heating rate of 10 K/min and a flow rate of 50 mL/min of 3% O_2 in argon. A quadrupole mass spectrometer (Balzers, MS-Cube 200) was used to analyze the product components during TPO. For the detection of O_2, CO, and CO_2 to the oxidation time, the intensities at m/e=32, 28, 44 were monitored, respectively. X-ray powder diffraction patterns were recorded by a Rigaku D-Max-IIIA diffractometer with CuKα radiation to examine the bulk structure of Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 catalysts.

RESULTS AND DISCUSSION

1. Activity of Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 Catalysts for RWReaction

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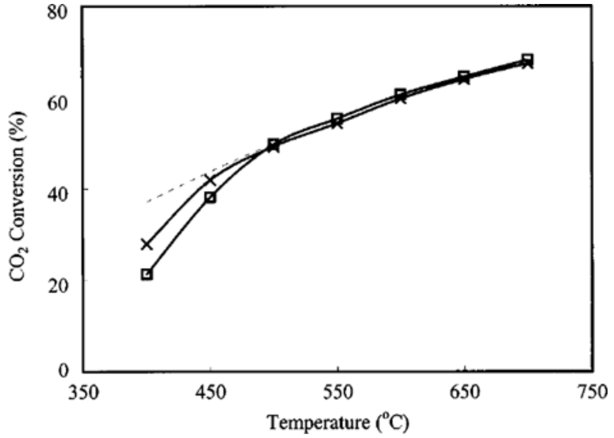

Fig. 1. CO_2 conversion vs temperature in RWReaction over Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 catalysts at GHSV (ml/g_{cat} · h) of 15,000.
------ Equil, —×— : FeCr(9 : 1), —□— : ZnCr(1 : 1)

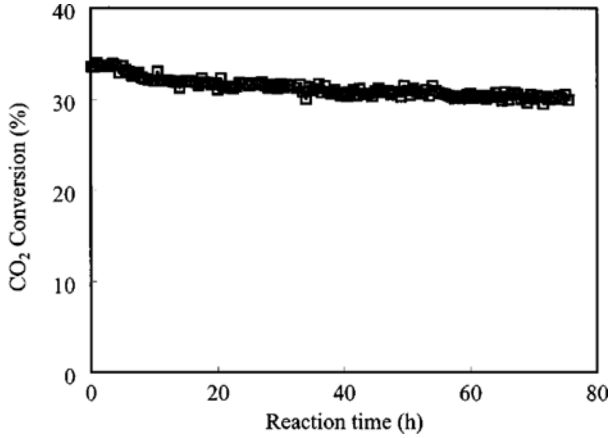

Fig. 2. CO_2 conversion vs reaction time over Fe_2O_3/Cr_2O_3 catalyst at 873 K and GHSV (ml/g_{cat} · h) of 100,000.

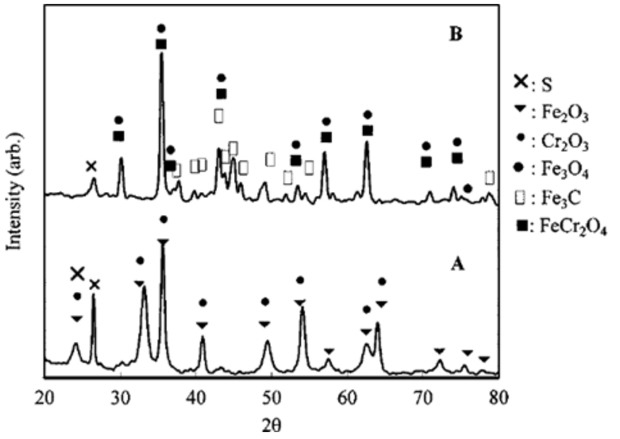

Fig. 3. XRD spectra of Fe_2O_3/Cr_2O_3 catalyst.
A: fresh catalyst, B: used catalyst

The RWReaction was carried out in a tubular quartz reactor (3/8" o.d.) to monitor the activities of Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 catalysts. The Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3 catalysts showed good activities for the RWReaction at the temperature range of 673-973 K and GHSV (ml/g_{cat} · h) of 15,000. Fig. 1 indicates the conversion of CO_2 vs temperature in the RWReaction. Two catalysts, Fe_2O_3/Cr_2O_3 and ZnO/Cr_2O_3, show good activity for the RWReaction of the CAMERE process. The activities of two catalysts were quite high so that the conversion reached close to the equilibrium at temperatures above 773 K. The RWReaction is endothermic, and hence the CO_2 conversion to CO is favored at high reaction temperature. In the CAMERE process, the methanol productivity markedly increased by the increment of CO concentration in the feed gas of the methanol synthesis reactor, which was dependent on the conversion of CO_2 in the RWReaction [Park et al., 2000]. This means that high catalyst activity for the RWReaction is important for the optimization of the CAMERE process.

2. Stability of Fe_2O_3/Cr_2O_3 Catalyst for RWReaction

The stability of Fe_2O_3/Cr_2O_3 catalyst was tested at 873 K with GHSV (ml/g_{cat} · h) of 100,000. The reaction environment in the RWReaction was very reductive with excess H_2 and high reaction temperature of 873 K. Such a strong reductive condition could easily reduce a metal oxide to the metal state, which was one of the reasons for the catalyst deactivation [Jung et al., 1995, 2000]. It was important to study the RWReaction under such a reaction condition, especially at high space velocity to monitor the stability in a short period of time. Fig. 2 shows the conversion of CO_2 over the Fe_2O_3/Cr_2O_3 catalyst with reaction time. The activity of the catalyst gradually decreased from 33.5 to 29.8% in the reaction period of 75 h. This indicates that the Fe_2O_3/Cr_2O_3 catalyst is not a good candidate for the RWReaction of the CAMERE process, although the Fe_2O_3/Cr_2O_3 is a well-known catalyst for high temperature water-gas-shift reactions.

X-ray powder diffraction patterns were recorded to investigate the transformation of the Fe_2O_3/Cr_2O_3 catalyst after the lifetime test. Fig. 3 shows the XRD spectra of the Fe_2O_3/Cr_2O_3 catalyst before and after the durability test for 75 h. The XRD spectrum of the fresh catalyst indicates the presence of S, Fe_2O_3, and Cr_2O_3 phases (Fig. 3A). However, after the reaction of 75 h, the Fe_2O_3 phase disappeared as well as Cr_2O_3 (Fig. 3B). All the Fe_2O_3 and Cr_2O_3 phases were reduced to Fe_3O_4 and $FeCr_2O_4$ phases after the RWReaction. The iron carbide of F_3C was also produced during the RWReaction. A part of Fe_2O_3 oxide might have been reduced to the Fe metal under the reaction conditions, which was known as an active site for the formation of CH_4 and coke in the water-gas-shift reaction [Twigg, 1989; Yan et al., 1999]. The coke formation on the Fe_2O_3/Cr_2O_3 catalyst used was confirmed by using TPO after a 75 h durability test. Fig. 4 shows the mass intensity spectra of O_2 (m/e=32) and CO_2 (m/e=44) during the TPO. The m/e=28 was also chased by a mass detector to monitor the occurrence of CO, but there was no trace of CO during the TPO. The carbon deposited on the used Fe_2O_3/Cr_2O_3 catalyst started to be oxidized from 643 K and was fully burned at 873 K, which indicates that coke was deposited during the RWReaction, causing the deactivation of the Fe_2O_3/Cr_2O_3 catalyst.

The effect of the coke formation on the Fe_2O_3/Cr_2O_3 catalyst surface was investigated in a large-scale reaction system. The CAMERE process for the methanol synthesis was operated on a production scale of 5 kg methanol per day, and then the process was simulated based on the data. The Fe_2O_3/Cr_2O_3 catalyst of 80 g was load-

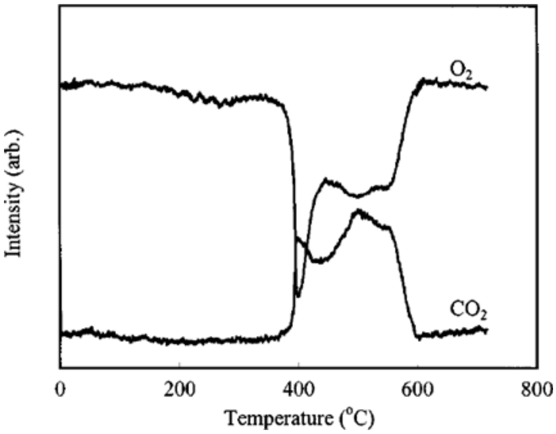

Fig. 4. TPO spectra of Fe_2O_3/Cr_2O_3 catalyst after RWReaction for 60 h. Sample=30 mg, heating rate=10 K/min, 3%O_2+Ar= 50 ml/min.

ed in a tubular reactor (1" o.d.) with an electric heater. The particle size of the catalyst was 0.2-0.3 mm. The RWReaction was carried out at 873 K and GHSV of 3,000 for 60 h to investigate the activity and the selectivity of the Fe_2O_3/Cr_2O_3 catalyst. The deactivation of the Fe_2O_3/Cr_2O_3 catalyst was not observed up to 60 h. But the RWReactor started to clog with the coke formed, and then the pressure of the RWReactor increased during the operation. As the pressure of the RWReactor increased, the CO selectivity continually decreased to 98% with CH_4 formation. The CH_4 formation in the RWReactor gave rise to a decrease of the partial pressure of reactant gases in the methanol reactor of the CAMERE process, decreasing the methanol productivity [Twigg, 1989]. The formation of coke and CH_4 on a catalyst should be prevented in the RWReaction of the CAMERE process. Therefore, the Fe_2O_3/Cr_2O_3 catalyst, which is a well-known catalyst for a water-gas-shift reaction, was not a suitable choice for the RWReaction of the CAMERE process.

3. Stability of ZnO/Cr_2O_3 Catalysts

To minimize the coke formation and to maximize a catalyst life, a new type catalyst of ZnO/Cr_2O_3 was investigated. One of the main reasons for coke formation on Fe_2O_3/Cr_2O_3 catalyst was the reduction of the iron oxide. Therefore, a logical choice would be ZnO, which formed a stable spinel structure of $ZnCr_2O_4$ with Cr_2O_3 [Cavani et al., 1991]. The ZnO/Cr_2O_3 catalysts showed good activity close to the equilibrium conversion even at a high space velocity. The conversion of CO_2 was higher than that of Fe_2O_3/Cr_2O_3 catalyst. It is important to note that the activity of ZnO/Cr_2O_3 catalysts at GHSV of 150,000 was considerably higher than that of Fe_2O_3/Cr_2O_3 catalyst at GHSV of 100,000. The stability of ZnO/Cr_2O_3 catalyst was tested at 873 K and GHSV of 150,000 (Fig. 5). The ZnO/Cr_2O_3 catalyst was stable for the RWReaction up to 120 h. The operation for 120 h at GHSV of 150,000 meant 10 months operation in real operating conditions for the CAMERE process. Those results presented above suggest that ZnO/Cr_2O_3 catalyst would be a proper choice for the RWReaction of the CAMERE process.

An X-ray diffraction experiment was performed to examine the transformation of a ZnO/Cr_2O_3 catalyst after the lifetime test. The XRD spectrum shows that the catalyst is a mixture of ZnO and $ZnCr_2O_4$ phases (Fig. 6). There was no phase change before and

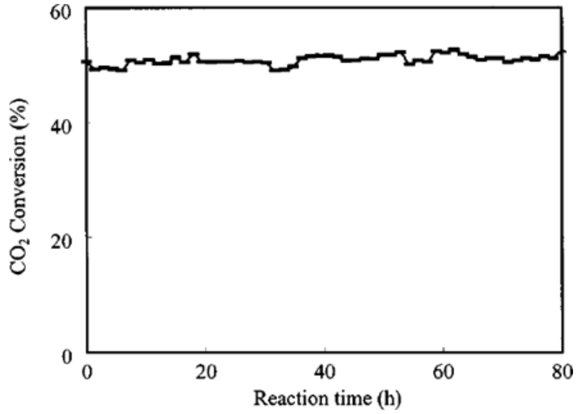

Fig. 5. CO_2 conversion vs reaction time on ZnO/Cr_2O_3 catalysts at 873 K and GHSV (ml/g_{cat} · h) of 150,000.
-: Zn : Cr=2 : 1, ×: Zn : Cr=1 : 1

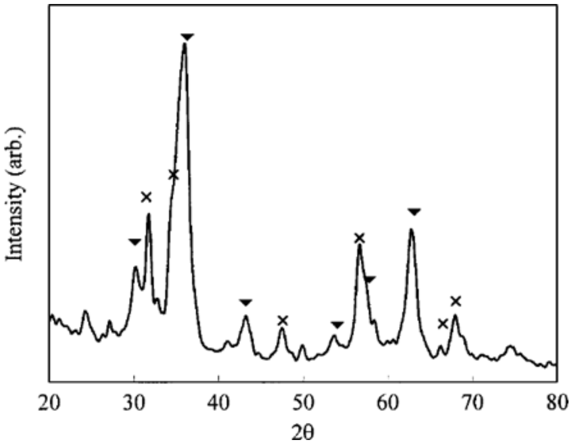

Fig. 6. XRD spectrum of ZnO/Cr_2O_3 catalyst.
×: ZnO, ▼: $ZnCr_2O_4$

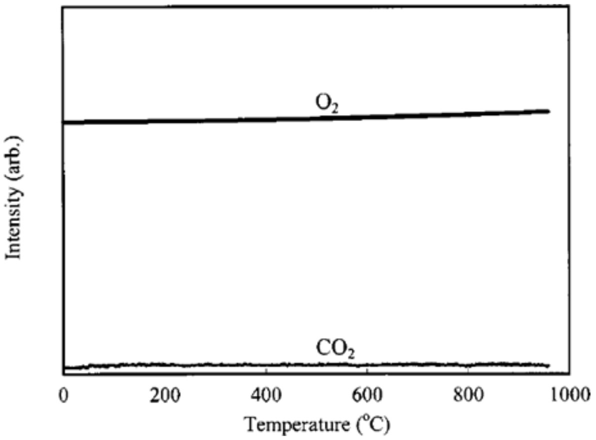

Fig. 7. TPO spectra of ZnO/Cr_2O_3 catalyst after RWReaction for 120 h. Sample=70 mg, heating rate=10 K/min, 3%O_2 in argon=50 ml/min.

after the durability test. TPO of the ZnO/Cr_2O_3 catalyst used was carried out to check the possibility of coke formation after the RWReaction for 120 h. Fig. 7 shows the intensity spectra of O_2 and CO_2 during the TPO. It is important to note that there was no CO_2

production, indicating the presence of coke on the catalyst surface. As a catalyst for the RWReaction of the CAMERE process, coke formation is fatal. The ZnO/Cr_2O_3 catalyst is a good catalyst for the RWReaction of the CAMERE process.

CONCLUSIONS

A ZnO/Cr_2O_3 catalyst was developed for the RWReaction of the CAMERE process. The activity of the catalyst was stable during the RWReaction and there was no coke formation. On the other hand, the well-known catalyst for a water-gas-shift reaction, Fe_2O_3/Cr_2O_3, was markedly deactivated during the RWReaction. The conversion of CO_2 on the Fe_2O_3/Cr_2O_3 catalyst decreased from 33.5 to 29.8% for 75 h at 873 K. The deactivation of the Fe_2O_3/Cr_2O_3 catalyst was attributed to the reduction of the metal oxide to the Fe metal, which also caused coke formation on the catalyst surface.

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