Selective Isobutene Formation in the CO Hydrogenation over Cs-doped ZrO_2

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(Received December 3, 1996)

The CO hydrogenation over Cs-doped ZrO_2 catalyst has been investigated for the direct synthesis of isobutene from synthesis gas. The Cs-doping by the deposition of metallic Cs remarkably enhanced only the isobutene production over ZrO_2, while the Cs-doping by CsOH decreased the catalytic activity of ZrO_2.

The development of a viable synfuel on catalyst has been anticipated since the oil crisis due to the demand of the products involving branched hydrocarbons. In many catalysts to produce hydrocarbons from synthesis gas, ZrO_2 catalyst is attractive since this metal oxide catalyst can directly synthesize branched hydrocarbons from synthesis gas.[1] We have reported that the CO hydrogenation over ZrO_2 at ca. 650 K selectively produces isobutene (selectivity > 80%) which is one of important materials for industry.[2-4] However, ZrO_2 catalysts for isobutene synthesis have not yet been practicable since the catalytic activity is too low. In order to improve the activity of ZrO_2, it is necessary to increase the activity or amount of active sites on ZrO_2.

We here describe the CO hydrogenation over Cs-doped ZrO_2 (Cs/ZrO_2) which exhibited a three times larger yield of isobutene and a higher isobutene selectivity than bare ZrO_2. Cs has the lowest work function in all metals, and Cs adsorbed on to surfaces acts as a strong electron donor. It has been known that Cs-doping on catalysts remarkably enhances some catalytic reactions.[5,6] However, CO hydrogenation has not yet been attempted over Cs/ZrO_2.

Two different kinds of catalysts, Cs/ZrO_2 and ZrO_2 impregnated with CsOH (CsOH/ZrO_2) for comparison purpose, were prepared from the ZrO_2 catalyst (monoclinic structure) with a specific surface area of 42 $m^2\ g^{-1}$. The preparation of the monoclinic ZrO_2 catalyst has been described elsewhere.[2-4] In the former case, Cs-doping was carried out in a Pyrex test tube connected to a vacuum line (< 0.1 Pa). The ZrO_2 powder (5 g) was soaked for 6 h at 373 K in the melting metallic Cs (5.0 g, KANTO CHEMICAL CO., INC.) which was taken out of the shield bottle in the test tube under vacuum, and then the mixture of ZrO_2 and Cs was heated under vacuum for 6 h at 673 K. In order to remove Cs species that were weakly bound to the surface, Cs/ZrO_2 cooled to room temperature under vacuum was soaked in ethanol (0.1 dm^3), and washed copiously with water in air until the washings were ca. pH 7. In the second case, ZrO_2 (5.0 g) impregnated with CsOH (0.5 g) using aqueous CsOH solution was heated at 673 K for 1 h in air, and evacuated in the test tube at 673 K for 6 h (< 0.1 Pa). The sample was then washed in a similar manner as above. The specific surface areas of Cs/ZrO_2 and CsOH/ZrO_2 were 50 and 45 m^2g^{-1}, respectively. These results show that there are no noticeable differences among the surface areas of ZrO_2, Cs/ZrO_2 and CsOH/ZrO_2. These catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and energy dispersive X-ray analysis (EDX), respectively. The CO hydrogenation over these catalysts at 643 K was investigated using a conventional flow system ($CO/H_2/N_2$= 2/2/1, total flow rate: 100 cm3 min-1).[2-4] Products were analyzed by an on-line gas chromatograph equipped with thermal conductivity detector, flame ionization detector, and three kinds of columns (P1, 5A molecular sieve, and VZ-10). Hydrocarbons and the isomers of C4 hydrocarbons were separated by P1 and VZ-10 columns, respectively.

Table 1 shows the yields and selectivities of produced hydrocarbons in the CO hydrogenation over ZrO_2, Cs/ZrO_2, and CsOH/ZrO_2. Oxygenates were not produced at this temperature.[2] The results in Table 1 were obtained in the steady-state that was reached within 2-5 h after the beginning of the reaction. In the reaction, the yield of CO_2 in each catalyst was far lager than that estimated by the total yield of hydrocarbons, whereas the formation of H_2O was not observed.[2,3] The formation rates of CO_2 in the steady-state are also listed in Table 1. It has been reported that methoxy and formate species are formed on the metal oxide surfaces such as ZrO_2 and CeO_2 in the CO hydrogenation.[2] These surface species are regarded as key intermediates leading to the hydrocarbons, while they are also decomposed into CO_2, CO, H_2O, and H_2 through formate or carbonate species above 573 K.[7,8] As a result, the decomposition of methoxy or formate species parallel to the formation of hydrocarbons is expected to produce CO_2 in quantity. Futhermore, the formation of CO_2 by the water-shift type reaction between CO and H_2O may result in no detection of H_2O after the reactor. As shown in Table 1, the CO hydrogenation over ZrO_2 selectively produced isobutene (80% in the total yield of hydrocarbons), while the production of alkane was little observed.[2,3] On the other hand, the formation

Table 1. Hydrocarbon yield in CO hydrogenation

Catalyst	ZrO_2	Cs / ZrO_2	CsOH / ZrO_2
Hydrocarbon yield /μmol min^{-1}			
CH_4	—	—	—
C_2H_6	—	—	—
C_2H_4	0.36 (9 %)[a]	0.30 (3 %)	0.09 (9 %)
C_3H_8	—	—	—
C_3H_6	0.24 (6 %)	0.30 (3 %)	0.05 (5 %)
C_4H_{10}	—	—	—
1-butene	0.04 (1 %)	—	0.02 (2 %)
trans-2-butene	0.04 (1 %)	—	0.01 (1 %)
cis-2-butene	0.04 (1 %)	—	0.01 (1 %)
isobutene	3.20 (80 %)	9.40 (94 %)	0.82 (82 %)
C5+[b]	0.08 (2 %)	—	—
Total	4	10	1
CO_2[c]	49	79	23

[a] The number in parenthesis represents selectivity.
[b] Hydrocarbons more than C5.
[c] Formation rate of CO_2/μmol min^{-1}.

rate of isobutene in Cs/ZrO_2 was about three times as high as that in ZrO_2. It is important to note here that the formation rates of C_2H_4 and C_3H_6 in Cs/ZrO_2 are almost equivalent to those in ZrO_2, respectively and C4 hydrocarbons except for isobutene were little produced in the reaction over Cs/ZrO_2. This implies that the Cs-doping in ZrO_2 enhances only the isobutene formation in the production of hydrocarbons. On the contrary, CsOH/ZrO_2 had a significantly lower activity than ZrO_2 although the hydrocarbon distribution with CsOH/ZrO_2 was almost the same as that of ZrO_2. Each catalyst had been maintaining the activity and selectivity over 50h.

Figure 1 shows the XPS spectra of ZrO_2 and Cs/ZrO_2 before the CO hydrogenation. The small peaks of Cs $3d_{5/2}$ and $3d_{3/2}$ (724 and 738 eV), which were attributed to Cs^+, were observed in the XPS spectrum of Cs/ZrO_2. Further washing of Cs/ZrO_2 with a large quantity of water (1 dm^3) resulted in no recognizable change of the XPS spectrum. These results imply that Cs^+ species on Cs/ZrO_2 are not water soluble. The atomic ratio of Cs to Zr (Cs/Zr) on the surface was roughly estimated at 0.023 (2.3%) from the peak intensities (peak areas) and the ionization cross sections (Cs: 22.93, Zr: 4.33) of Cs $3d_{5/2}$ and Zr $3d_{5/2}$. There were no remarkable differences between the XPS spectra of ZrO_2 and Cs/ZrO_2 around the valence band. On the other hand, Cs species were not observed in a XPS spectrum of CsOH/ZrO_2. There were no noticeable differences among the XRD patterns of ZrO_2, Cs/ZrO_2, and CsOH/ZrO_2 that represented the monoclinic structure of ZrO_2. The EDX analysis detected only the signal of Zr (2.04 eV, $L\alpha_1$) in ZrO_2 and CsOH/ZrO_2, while the weak signal (4.29 eV, $L\alpha$) due to Cs in addition to the signal of Zr was observed in the Cs/ZrO_2. On the basis of the peak intensities of Zr $L\alpha_1$ and Cs $L\alpha$ that were observed in the ZrO_2 catalyst and a metallic Cs film prepared by the Cs deposition, respectively, the Cs concentration in Cs/ZrO_2 was estimated at 0.09 - 0.15%. The estimation is much smaller than that by XPS. This may reflect that most of Cs^+ in the Cs/ZrO_2 exists on the surface since EDX is has a deeper analysis depth than XPS. It is difficult to consider Cs^+ ion to bind to ZrO_2 as charge transfer complexes on Cs/ZrO_2. If such Cs species had been formed on Cs/ZrO_2, the copious washing with water would have removed the Cs species from the surface. In Cs/ZrO_2, water insoluble Cs compounds such as cesium zirconate Cs_2ZrO_3 may be formed on a part of ZrO_2 surface. Alkali zirconates, which are generally prepared by the reaction of ZrO_2 and melting alkali salts, are insoluble in water. Although we have not yet understood the structure and characteristics of the Cs species on Cs/ZrO_2, the surface Cs species are expected to be formed by the direct reaction between metallic Cs and ZrO_2 since there are no such Cs species on CsOH/ZrO_2 as shown in the results of the reaction and XPS.

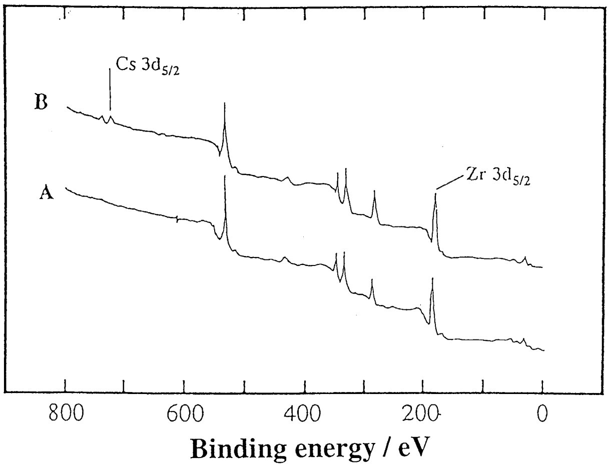

Figure 1. XPS spectra of ZrO_2 and Cs/ZrO_2.
A: ZrO_2 B: Cs/ZrO_2. The binding energy was corrected by Au (Au $4f_{7/2}$, 83.8 eV) deposited on the catalysts.

We can draw a conclusion from above results; the Cs^+ ion species formed on ZrO_2 surface remarkably promotes the production of isobutene in the CO hydrogenation over ZrO_2. This is not attributed to the surface area of Cs/ZrO_2 since each catalyst has similar surface areas. It is more probable that Cs/ZrO_2 have a lager number of active sites or more activated sites in the unit surface area than ZrO_2. Isosynthesis in the CO hydrogenation over metal oxide catalysts have been investigated.[9,10] These studies indicate that branched hydrocarbons are formed on the basic sites. However, the increase of the basic sites alone cannot explain the activity and selectivity of isobutene in Cs/ZrO_2 since the simple increase of the basic sites on Cs/ZrO_2 would enhance the yields of other alkenes in addition to isobutene. As a result, the activation of the specific basic sites for isobutene formation or the increase of the activated specific sites may cause the activity of Cs/ZrO_2. It is important to note the CO_2 yield in each catalysts. As shown in Table 1, the CO_2 yield is ca. 8 times as great as that of hydrocarbons in Cs/ZrO_2. This is smaller than the case of CsOH/ZrO_2 (23 times) with the poor activity, suggesting that Cs/ZrO_2 has a smaller activity for the decomposition of methoxy or formate species parallel to the formation of hydrocarbons than ZrO_2 and CsOH/ZrO_2. Although it has not yet been clear whether Cs^+ ion species itself or electron donation from Cs to the basic sites on ZrO_2 surface are the active sites for the isobutene formation, the characteristics of the specific active sites will be available for understanding the CO hydrogenation over ZrO_2 which mainly produces isobutene.

This study revealed that Cs-doping in ZrO_2 remarkably enhanced the isobutene formation in the CO hydrogenation over ZrO_2. This may lead to the available catalysts for the direct-isobutene synthesis from synthesis gas. The details of Cs/ZrO_2 are under investigation.

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