Dependence of Catalytic Activity in CO Hydrogenation on Strong Basic Sites of ZrO_2 Surface

Lianhai Lu, Tomoki Hayakawa, Tetsuji Ueda, Michikazu Hara, Kazunari Domen, and Ken-ichi Maruya*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received September 29, 1997; CL-970744)

Thermal desorption (TD) study on CO_2-adsorbed ZrO_2 showed that the activity of ZrO_2 in isosynthesis of isobutene from CO+ H_2 is closely related to the strong basic sites on its surface.

Zirconium dioxide (ZrO_2) has been attracting much attention due to its special function as a catalyst for activation and conversion of C-H, C=O and H-H bonds, and also as a useful support for preparing versatile catalysts. Especially, ZrO_2 was found to be a selective catalyst for the direct synthesis of isobutene from CO+ H_2 with reasonable conversion at about 670 K.[1-10] Though extensive studies on ZrO_2 have been made,[11-15] the relationship between hydrocarbon formation in CO+ H_2 reaction and the basic sites is not yet understood. This paper report the thermal desorption (TD) study on CO_2-adsorbed ZrO_2.

Hydrous zirconia (ZrO_2 precursor) was prepared from the hydrolysis of zirconium oxynitrate ($ZrO(NO_3)_2 . 2H_2O$) by slowly adding 100 ml 5 wt% ammonia aqueous solution to 500 ml zirconium oxynitrate aqueous solution (0.187 M) under vigorous stirring. Three kinds of catalysts (ZrO_2-a,b,c) were prepared from this precursor. ZrO_2-a was prepared by washing the precursor with distilled water, drying in air at 393 K for 8 h, and then calcining at 723 K for 3 h in air flow. ZrO_2-b was obtained by drying and heating the precursor without water washing and ZrO_2-c by ball-milling the precursor for 15 min, following drying and heating in the same manner as above. One of ZrO_2 catalyst (ZrO_2-d) was prepared by aging the hydrolysis product from zirconium oxynitrate in the solution at 373 K for 60 h and then drying and calcining in the same way as above. The CO-H_2 reaction over ZrO_2 catalysts (2 g) was carried out at 673 K and atmospheric pressure in a conventional flow reaction system (N_2 : CO : H_2 = 1: 2 : 2, total flow rate: 100 ml min^{-1}). Products were analyzed by an on-line gas chromatograph. The TD experiments with 0.4 g of ZrO_2were carried out in a flow system with He as carrier gas at a flow rate of 50 ml min^{-1}. High purity CO_2 was quantitatively fed into the system by mass flow controller. Temperature was linearly increased at a rate of 20 K min^{-1}. Before starting TD experiment, the ZrO_2 sample was in-situ pretreated at 773 K for 3 h and then 863 K for 30 min under He blowing. XRD analysis shows that both monoclinic and tetragonal structure exist on each ZrO_2. The TD effluents were directly analyzed by an on-line gas chromatograph. Mass analysis proved that only CO_2 and small amount of H_2O existed as desorbents.

Table 1 shows the BET specific surface areas of the prepared ZrO_2 catalysts and the reaction results in the CO-H_2 reaction over each catalyst. No oxygenates was detected under the reaction conditions. It is known that the preparation method for ZrO_2-d results in large surface area ZrO_2[15]. On the other hand, ball-milling the precursor also produce large surface area ZrO_2-c. It is interesting that though ZrO_2-c and -d have larger surface areas than ZrO_2-a and -b, the total yield of hydrocarbons decreases in a sequence of a>b>c>d with high isobutene selectivity. This indicates that the catalytic activity of ZrO_2 is not simply dependent on the surface area but the amount and/or the characteristics of active sites determine the catalysis.

Table 1. Activity and Selectivity of ZrO_2 Catalysts

ZrO_2	BET S. A. $m^2\ g^{-1}$	Formation rate $\mu mol\ min^{-1}$ total H.C.	CO_2	C_4 selectivity/ C-base% (isobutene/total C_4)
a	75	0.73	1.91	78(95)
b	76	0.55	1.90	80(95)
c	101	0.28	1.80	73(92)
d	155	0.07	0.94	62(100)

In order to investigate the basic sites on ZrO_2 surface, TD spectra of each catalyst were measured. Figure 1 shows the TD spectra of ZrO_2-a exposed to different amount of CO_2 at 300 K. At low exposure (30μmol), a maximum desorption peak is observed at 680 K. As the exposure increases, the maximum desorption peak shifts gradually to lower temperature. When the ZrO_2 surface is completely saturated by CO_2 (210 μmol exposure) the maximum desorption peak of CO_2 is observed at 420 K, and in addition, a side peak at about 680 k obviously appears, indicating that the ZrO_2 surface is not homogeneous. It is well known that CO_2 adsorbed onto strong basic sites of metal oxides desorbs at higher temperatures, while that adsorbed on weak

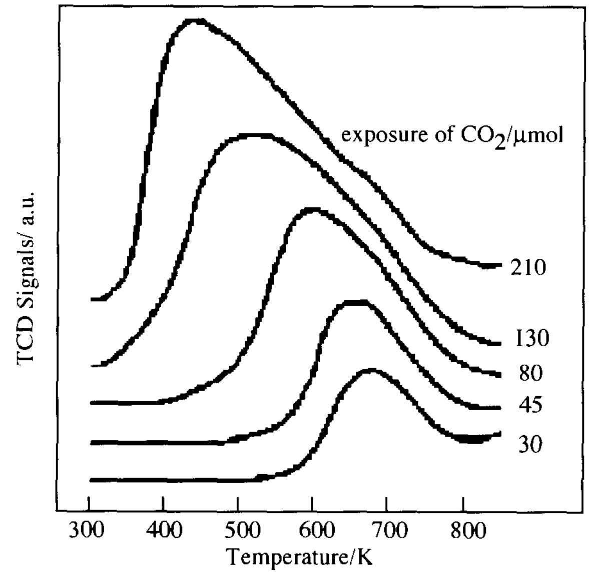

Figure 1. TD spectra of ZrO_2 treated with CO_2 at different exposure.

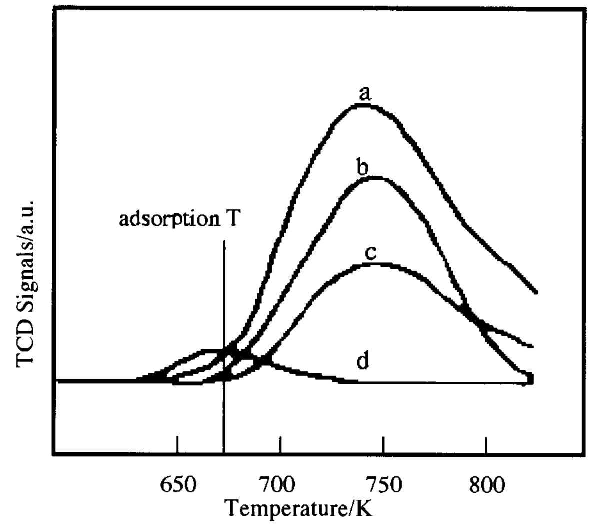

Figure 2. TD spectra of 4 kinds of ZrO_2 adsorbed by CO_2 to saturation at 673K. CO_2 desorption amount/µmol.g-1: a:60, b:48, c: 23, d: trace.

basic sites desorbs at lower one.[13,14] Therefore, it can be concluded that there are several kinds of basic sites on ZrO_2 and the desorption peak at about 680 K, which was also observed at low exposure, is expected to be the desorption of CO_2 adsorbed on the stronger basic sites.

Since the TD peaks of ZrO_2 saturatedly treated at 300K are too large and broad, it is difficult to discuss the detail of each TD spectrum. Therefore, we studied the TD spectra of ZrO_2 which adsorbed CO_2 at various temperatures. Figure 2 shows TD spectra of ZrO_2-a, -b, -c, and -d exposed to 100 µmol CO_2 at 673 K, under which conditions the surface of all of ZrO_2 was completely saturated by CO_2. Each spectrum was obtained by introducing CO_2 to the system at 673K, keeping the temperature constant for 1 h under He blowing to completely remove any free CO_2 in the system, cooling down the system to 300 K and then starting the TD experiment. The TD spectra of ZrO_2-a, -b, and -c have a similar type of broad desorption peak at 680-830 K but with quite different peak intensity, while ZrO_2-d has no peak corresponding to this temperature region. The desorption amount of CO_2 decreases from 60µmol to trace in the sequence of a>b>c>d, which means there are different amount of strong basic sites on those catalyst surfaces. This sequence is in good agreement with that of the hydrocarbon formation rate and C_4 yield, as illustrated in Table1. This indicates that the strong basic sites which are strong enough to adsorb CO_2 at reaction temperature (673 K) can be related to its catalytic activity. Consequently, the reaction data can be well explained by the TD results: though ZrO_2-c and ZrO_2-d have high surface areas, there are fewer strong basic sites on their surfaces as shown in Fig.2, and therefore, their activities are lower than that of ZrO_2-a and ZrO_2-b. Although we have not yet understood the structure or chemical properties of the strong basic sites, it is probable that some structure in the precursor formed by the hydrolysis of zirconium oxynitrate leads to the active basic sites after calcination since the treatment of the precursor before calcination considerably determines the nature and/or the amount of the basic sites as well as the catalytic activity. It is therefore inferred that a key point of improving activity and selectivity of zirconia in one step isosynthesis of isobutene is to increase the strong surface basic sites by modifying the preparation method. The influence of the preparation method of ZrO_2 precursor on the basic sites are now under further investigation.

References and Notes

1 M.-Y. He and J. G. Ekerdt, *J. Catal.*, **87**, 239(1984).
2 H. Maehashi, K. Maruya, K. Domen, K. Aika, and T. Onishi, *Chem. Lett.*, **1984**, 747.
3 K. Maruya, A. Inaba, T. Maehashi, K. Domen, and T. Onoshi, *J. Chem. Commun.*, **1985**, 487.
4 K. Maruya, T. Maehashi, T. Haraoka, S. Narui, K. Domen, and T. Onishi, *J. Chem. Commun.*, **1985**, 281.
5 J. Kondo, H. Abe, Y. Sakata, K. Maruya, K. Domen, and T. Onishi, *J. Chem. Soc., Faraday Trans.*, **84**, 511 (1988).
6 K. Maruya, T. Fujisawa, A. Takasawa, K. Domen, and T. Onishi, *Bull. Chem. Soc. Jpn.*, **62**, 11(1989).
7 N. B. Jackson and J. G. Ekerdt, *J. Catal.*, **31**, 126(1990).
8 K. Maruya, *J. Japan Petroleum Institute*, **37**, 246(1994).
9 K. Maruya, *Catal. Lett.*, **24**, 349(1994).
10 K. Maruya, A. Takasawa, M. Aikawa, T. Haraoka, K. Domen, and T. Onishi, *J. Chem. Soc., Faraday Trans.*, **90**, 911(1994).
11 J. Lamotte, V. Moravek, M. Besitel, and J.-C. Lavalley, *React. Kinet. Catal. Lett.*, **36**, 113(1988).
12 C. Morterra, L. Orio, and C. Emanuel, *J. Chem. Soc., Faraday Trans.*, **86**, 3003(1990).
13 B.Q. Xu, T. Yamaguchi, and K. Tanabe, *Chem. Lett.*, **1996**, 945.
14 H. Nakabayashi, *Chem. Lett.*, **1996**, 945.
15 G.K.Chuah, S.Jaenicke, S.A.Cheong, and K.S.Chan, *Appl. Catal. A: General*, **267**, 145(1996).