Linear Relationship of the Rate of Isobutene Formation from CO and H_2 on ZrO_2 to the Monoclinic Phase Fraction

Ken-ichi Maruya,* Teruaki Komiya, Koichiro Okumura, and Masatomo Yashima†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503
†*Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering,*
Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502

(Received March 29, 1999; CL-990232)

The rate of formation of isobutene from CO and H_2 over ZrO_2 is proportional to the volume fraction of the monoclinic phase. The active site was explained by both vacant site and stronger bascity due to the shorter Zr-O bond in the monoclinic structure.

The formation of isobutene in the CO hydrogenation was first reported using oxide catalysts such as ThO_2 under very severe conditions[1] and has been named as "Isosynthesis."[2] We have reported that ZrO_2, one of the "Isosynthesis" catalysts, is the most selective catalyst for the formation of isobutene from CO and H_2 under mild conditions.[3] Although there have been some mechanistic studies on the formation of branched chain compounds over oxide catalysts, [4-9] there has been no study on the active sites to our knowledge. In this paper, we describe the relation of the activity of isobutene formation from CO and H_2 to the bulk structures of ZrO_2 and discuss the active sites on the basis of the structures.

ZrO_2 catalysts were prepared by the precipitation method. ZrO_2 with different structure was prepared by controlling pH of mother liquid in the precipitation from aqueous zirconium nitrate solution with aqueous ammonia. The precipitate was washed with distilled water repeatedly, dried at 413 K overnight, and calcined at 723 K for 3 h. The volume fraction of monoclinic phase was estimated from X-ray diffraction profile using the equation after Toraya et. al.[10] The XRD spectra were recorded using step scan method in the range $2\Theta=21\text{-}37°$, step width=0.02° on an x-ray difractometer (MXP^{3VA}, MAC Science Co). X-Ray profile thus obtained was decomposed into $11\bar{1}_m$, 111_t and 111_m reflection peaks, assuming Peason VII-type functions(11), where m and t denote monoclinic and tetragonal phases. CO hydrogenation was carried out in a conventional flow system at 673 K and an atmospheric pressure.

Table 1 shows the rate of hydrocarbon formation and the selectivity of isobutene in CO hydrogenation over ZrO_2 prepared under several pH values of mother liquid in the solution of zirconium hydroxide. BET surface areas were almost constant at about 100 $m^2 \cdot g^{-1}$ except for ZrO_2 prepared at pH=2.1 and 4.5. The formation rates of total hydrocarbon and C_4 hydrocarbons, the selectivity of isobutene, and the volume fraction of monoclinic phase are highest in the catalyst of pH 10.5. C_4 hydrocarbons are main products and the selectivity of isobutene in C_4 hydrocarbons is more than 80%. Furthermore, the balance of total hydrocarbons and C_4 hydrocarbons is within 2 and 3 except for ZrO_2s of pH 2.1 and 13.0. To prepare ZrO_2 at pH 13, concentrated aqueous NaOH solution was used instead of aqueous NH_3 solution.

Table 1. Rate of hydrocarbon formation and selectivity of isobutene in CO hydrogenation with ZrO_2 prepared at several pH values[a]

pH value	Surface area / $m^2 \cdot g^{-1}$	Formation rate / $\mu mol.g^{-1}.h^{-1}$		Isobutene[b] / %	Mono-clinic[c] / %
		Total H.C.	C_4 H.C.		
2.1	15	0.6	0.4	84	4
4.5	40	7.4	5.7	88	50
6.0	109	9.3	7.1	91	45
7.0	110	10.6	8.6	94	70
9.0	111	13.1	10.6	94	84
10.5	110	13.6	11.2	94	88
13.0[d]	105	0.04	0	-[e]	0

[a]Catalyst: 2.0 g, reaction temperature: 673 K, flow rate: $CO/H_2/N_2=40/40/20$ $ml \cdot min^{-1}$. [b]Selectivity of isobutene in C_4 hydrocarbons. [c]Volume fraction of monoclinic phase in ZrO_2. [d]ZrO_2 was prepared using aqueous NaOH solution instead of aqueous ammonia. [e]C_4 hydrocarbons were not detected.

Figure 1 shows the relation of the formation rates of isobutene to the volume fraction of monoclinic phase. It is clear that the rate increases linearly with increasing the volume fraction of monoclinic phase. This strongly suggests that ZrO_2 with monoclinic phase is responsible for the formation of isobutene. Subtraction of formation rate of isobutene from that of total hydrocarbons is nearly 2 $\mu mol.g^{-1}.h^{-1}$ except for those with the catalysts prepared at pH values of 2.1 and 13. This indicates that the formation of hydrocarbons other than isobutene is independent of ZrO_2 with monoclinic phase.

Zr ions in tetragonal phase are surrounded by 8 oxygen ions with

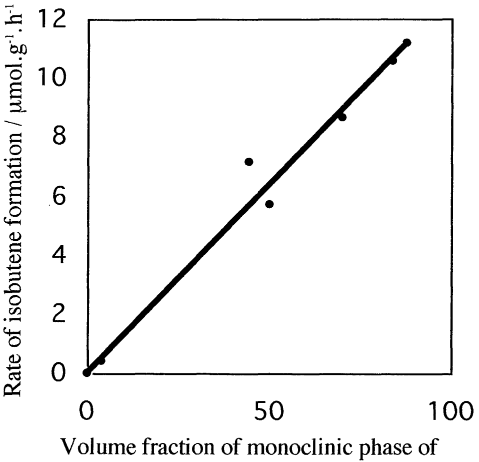

Figure 1. Relation of rate of isobutene formation to volume fraction of monoclinic phase of ZrO_2.

distorted fluorite-type structure, and each oxygen ion is surrounded by 4 zirconium ions.[12,13] On the other hand, Zr ion in the monoclinic structure has 7 oxygen ions in the coordination sphere.[12,13] The view from oxygen ions in monoclinic structure shows that 4 oxygen ions are in almost the same positions but remaining 3 oxygen ions are different, i.e., the 3 oxygen ions are surrounded by 3 Zr ions. This indicates that there is one coordinatively vacant coordination site on Zr ion in ZrO_2 with monoclinic structure. Although the above description on the coordination sites is based on the bulk structure, it is likely that the surface reflects the bulk structure. Thus, the higher activity on ZrO_2 with monoclinic structure shown in Figure 1 could be explained by the vacant site.

On the other hand, we have reported that the rate of isobutene formation over ZrO_2 increases with increasing the strongly basic sites.[14] The amount of the basic sites was nearly 40 μmol.g^{-1}. This amount corresponds to nearly 7% on the ZrO_2 surface, under the presumption that the structure is cubic and the surface area is 100 m^2.g^{-1}, indicating that the sites are not a kind of defects. Among seven oxygens in the monoclinic structure, each of four oxygen ions combines with four Zr ions in the same way to the tetragonal phase, while the remaining three oxygen ions in monoclinic structure have only three Zr ions in their coordination sphere.[12,13] The oxygen ions combining with three Zr ions naturally have the higher electron density than those with four Zr ions.

Thus, the higher activity on ZrO_2 with monoclinic structure would be attributed to the presence of the vacant site and the higher electron density .

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