ELSEVIER

Journal of Molecular Catalysis A: Chemical 159 (2000) 97–102

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Active sites on ZrO_2 for the formation of isobutene from CO and H_2

Ken-ichi Maruya [a,*], Teruaki Komiya [a], Tomoki Hayakawa [a], Lianhai Lu [b], Masatomo Yashima [c]

[a] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan*
[b] *Physical Chemistry Laboratory, School of Chemical Engineering, Dalian University of Technology, Zhongshan Road 158, Dalian, 116012, People's Republic of China*
[c] *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, Japan*

Abstract

The selective formation of isobutene from CO and H_2 over ZrO_2 has been investigated. ZrO_2 catalysts having different fraction of monoclinic phase were prepared by changing pH value in the mother solution at the precipitation of zirconium hydroxide. The rate of isobutene formation increased with an increase in the volumetric fraction of monoclinic phase in ZrO_2, while those of C_1, C_2, C_3, and C_5+ were independent of the fraction. The amounts of adsorbed methoxy and formate species during the reaction and also of the surface sites with strong basicity increased with an increase in the fraction of monoclinic phase. Chemical trapping experiment showed that the amount of surface methoxy species is comparable to that of site with the strong basicity. These findings were explained by both coordinate unsaturation and stronger basicity based on the configuration of ZrO_7 group in the monoclinic structure.

Keywords: CO hydrogenation; ZrO_2; Isobutene; Monoclinic structure; Active sites

1. Introduction

The formation of branched hydrocarbons 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]. As seen from the name, the CO hydrogenation over oxide catalysts forms exclusively branched compounds [2,3]. 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 [4]. Some mechanistic studies on the formation of branched chain compounds over oxide catalysts have been reported. Although the carbonylation at carbon of carbonyl intermediates has been proposed [5,6], aldol condensation-type reaction for the chain-branching has becoming the likely mechanism [7–10] and the key reaction has been proposed to be the formation of C_2 species, which is the start-

* Corresponding author. Tel.: +81-45-924-5239; fax: +81-45-924-5276.
E-mail address: kmaruya@res.titech.ac.jp (K.-i. Maruya).

1381-1169/00/$ - see front matter
PII: S1381-1169(00)00176-X

ing material in the condensation reaction [10,11]. The aldol condensation reaction is well known to proceed by the acid and base catalysts [12]. TPD spectra of CO_2 adsorbed at some temperatures showed that the formation of hydrocarbons, especially isobutene, over ZrO_2 is related to the sites with stronger basicity [13]. On the other hand, there has been no study on the active sites to form the branched chain compounds from CO and H_2 to our knowledge. In this paper, we describe the relation of rate of isobutene formation to the fraction of monoclinic phase and the properties of active sites on ZrO_2 with monoclinic structure and discuss the relation of the sites to the formation of isobutene from CO and H_2.

2. Experimental

ZrO_2 catalysts were prepared by the precipitation method. ZrO_2 with different structure was prepared by controlling pH of mother solution in the precipitation from aqueous zirconium oxynitrate solution with aqueous ammonia solution. The precipitate was washed with distilled water, dried at 413 K overnight, and calcined at 723 K for 3 h. The catalyst prepared at 9.0 of pH in the mother solution is denoted as ZrO_2(9.0).

CO hydrogenation was carried out using a conventional flow system at 673 K and an atmospheric pressure with a mixture of $CO/H_2/N_2 = 40{:}40{:}20$ ml min^{-1}.

The volume fraction of monoclinic phase was estimated from X-ray diffraction (XRD) profile using the equation after Toraya et al. [14,15]. The XRD spectra were recorded using step scan method in the range $2\Theta = 21–37°$, step width = 0.02° on an X-ray difractometer (MXP^{3VA}, MAC Science). X-ray profile thus obtained was decomposed into $\bar{1}11_m$, 111_t, and 111_m reflection peaks, assuming Peason VII-type functions(11), where m and t denote monoclinic and tetragonal phases.

Chemical trapping experiments were carried out as follows: The catalyst after several hour reaction was rapidly cooled by liquid nitrogen. After having cooled and evacuated at liquid nitrogen temperature, the catalyst was slowly warmed to room temperature under N_2. Then, the catalyst was dropped into a flask which contained 20 wt.% DCl at liquid nitrogen temperature. After evacuation, the catalyst in the flask was kept at room temperature overnight. The sample for ^{1}H NMR measurement was collected from the supernatant part at the top.

TPD experiments were carried out using a flow system equipped with quartz reactor placed 0.4 g of catalyst at a rate of 20° min^{-1} under He of 50 ml min^{-1}. The CO_2 adsorption was carried out with a flow of $He/CO_2 = 50{:}1.8$ ml min^{-1} for 15 min at 673 K, followed by a flow of He of 50 ml min^{-1} at the same temperature for 2 h to remove weakly adsorbed CO_2.

3. Results and discussion

3.1. Determination of monoclinic phase in ZrO_2

ZrO_2 usually consists of a mixture of monoclinic and tetragonal phases. XRD measurement shows the typical three peaks due to monoclinic and tetragonal phases in the region from 21° to 37°. The volumetric fraction of monoclinic phase estimated using the two peaks at 28.06° and 31.27° due to monoclinic phase and a peak at 30.28° due to tetragonal phase by the method of Toraya [11] is shown in Table 1 along with the surface area. Except for ZrO_2(13.0), the in-

Table 1
Volumetric fraction of monoclinic phase in ZrO_2

pH	Surface area (m^2 g^{-1})	Volumetric fraction of monoclinic phase (%)
2.1	15	4
4.5	70	50
6.0	109	45
7.0	110	70
9.0	111	84
10.5	110	88
13.0	105	0

crease in the value of pH leads to the increase of volumetric fraction in ZrO_2. The value of zero of volumetric fraction with ZrO_2(13.0) contains the error of about 1%. BET surface areas are almost constant except for ZrO_2(2.1) and ZrO_2(4.5), the yield of which were low and which, therefore, might not be compared to the other catalysts.

3.2. Relation of formation rate of isobutene to volumetric fraction of monoclinic phase in ZrO_2

Table 2 shows the rate of hydrocarbon formation over some ZrO_2 catalysts. The rates seem to depend on the pH values in the precipitation of zirconium hydroxides. The selectivities of isobutene in C_4 hydrocarbons and total hydrocarbons increase with an increase in the pH value except for ZrO_2(13.0). The extremely low activity with ZrO_2(13.0) may not be due to the effect of Na ion remaining on the surface, since ZrO_2 prepared at pH = 9 using NaOH or doped by Cs showed a high activity with very high selectivity to isobutene [16,17].

Fig. 1 shows the relation of the formation rate and the selectivity of isobutene to volumetric fraction of monoclinic phase in ZrO_2. The rate and the selectivity increase with an increase in the volumetric fraction of monoclinic phase in ZrO_2, suggesting that the monoclinic structure closely participates the active sites. On the other hand, formation rates of C_1, C_2, C_3, and C_5 hydrocarbons do not seem to have any relation to the volumetric fraction of monoclinic phase, as shown in Fig. 2. This suggests that the phase structure is not important for the formation of the other hydrocarbons than isobutene. As shown in Table 2, ZrO_2(13.0) shows very little activity for methane formation and no formation of higher hydrocarbons than C_3. Therefore, monoclinic structure seems to be essential for the formation of hydrocarbons from CO and H_2.

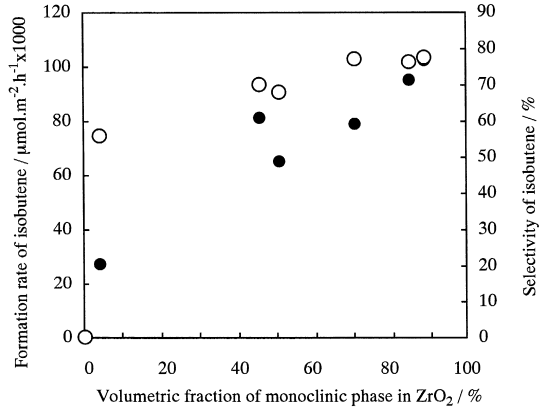

Fig. 1. Relation of formation rate and selectivity of isobutene in total hydrocarbons to volumetric fraction of monoclinic phase in ZrO_2. ● Formation rate of isobutene. ○ Selectivity of isobutene in total hydrocarbons.

Table 2
Rate of hydrocarbon formation over some ZrO_2 catalysts[a]

pH[b]	Rate of formation[c] (μmol m^{-2} h^{-1} × 1000)							Selectivity of isobutene[d] (%)	
	CO_2	Total HC	C_1	C_2	C_3	C_4	C_5 +	in C_4 hydrocarbons	in total hydrocarbons
2.1	210	40	+	10.0 (87)	4.7 (100)	27	0.7	84	56
4.5	160	106	3.7	6.7 (93)	4.9 (91)	81	8.4	88	68
6.0	129	84	3.9	5.0 (84)	3.9 (88)	65	6.7	91	70
7.0	151	96	1.7	3.9 (91)	4.5 (92)	79	7.5	94	77
9.0	110	118	3.1	5.4 (83)	5.7 (87)	95	8.5	94	76
10.5	145	124	2.4	5.1 (86)	5.8 (88)	102	8.3	94	77
13[e]	34	0.4	0.3	0.1 (100)	0 –	0	0	0	0

[a] Catalyst: 2.0 g, reaction temperature: 673 K.
[b] pH values with the mother solution in the precipitation from zirconium oxynitrate with aqueous ammonia solution.
[c] Parentheses are the selectivity of olefin.
[d] Isobutene selectivity in total and C_4 hydrocarbons.
[e] The ZrO_2 was prepared from zirconium oxynitrate with aqueous sodium hydroxide.

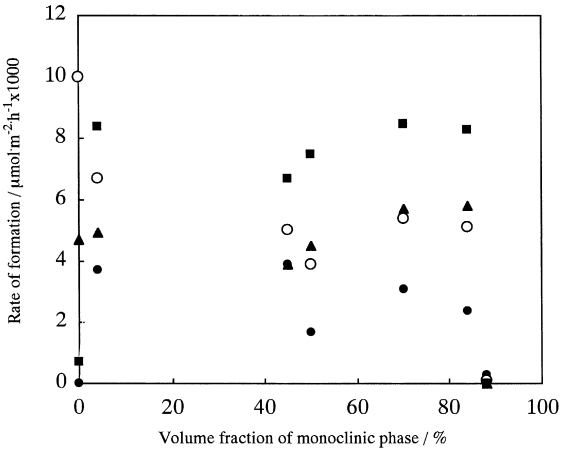

Fig. 2. Relation of rate of formation of C_1, C_2, C_3, and C_5+ hydrocarbons to volumetric fraction of monoclinic phase in ZrO_2. ● methane, ○ C_2 hydrocarbons, ▲ C_3 hydrocarbons, ■ C_5+ hydrocarbons.

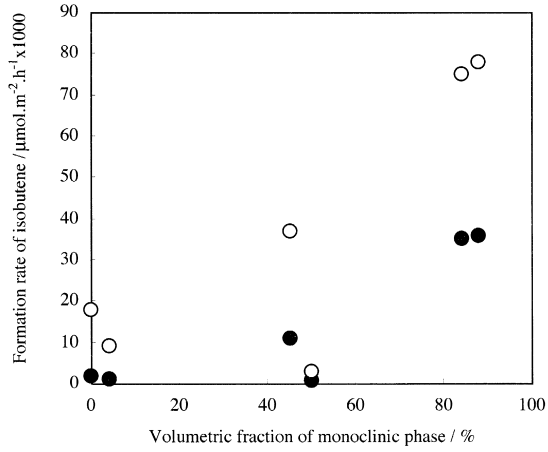

Fig. 3. Relation of amounts of surface methoxy and formate species to volumetric fraction of monoclinic phase in ZrO_2. ● Amount of methoxy species. ○ Amount of formate species.

3.3. Determination of surface species

To make clear the relation of phase structure to the formation of hydrocarbons, surface species during the reaction was investigated using chemical trapping method. The previous method was carried out by the treatment of catalyst after the reaction with a vapor of diluted hydrochloric acid, showing only the species of methoxy and formate [10]. Here, the method was improved so as to treat the catalyst with DCl–D_2O solution and the amounts of products were determined by ^1H NMR spectroscopy. Table 3 shows the amounts of surface methoxy and formate species along with the formation rate of isobutene. The relation of the amounts of methoxy and formate species to the volumetric fraction of monoclinic phase in ZrO_2 is shown in Fig. 3, where $ZrO_2(3.5)$ was selected instead of $ZrO_2(4.5)$. Except for the data of $ZrO_2(3.5)$, the amount increases with an increase in the fraction of monoclinic phase. This leads to the two possibilities: (i) methoxy and formate species are stable on the surface on the monoclinic structure, but not on the tetragonal, and (ii) the surface on monoclinic structure is active for the formation of methoxy and formate species, but that on tetragonal structure is inactive. To check this, $ZrO_2(2.1)$ and $ZrO_2(9.0)$ were treated with methanol and then with DCl–D_2O solution similarly to the chemical trapping as a preliminary experiment. The amounts of methanol obtained for both catalysts were almost the same, indicating that both structures have the ability to adsorb methoxy species. Therefore, the results in Fig. 4 support possibility (ii).

Table 3
Amount of surface species on some ZrO_2 catalysts

pH	Amount of surface species (μmol g^{-1})		Formation rate of isobutene (μmol g^{-1} h^{-1})
	methoxy	formate	
2.1	1	9	0.01
3.5	1	3	2.7
6.0	11	37	7.2
9.0	35	75	10.6
10.5	36	78	11.2
13.0	2	18	0

3.4. Difference between monoclinic and tetragonal phases

Zr atoms in tetragonal phase are surrounded by eight oxygen atoms with a distorted fluorite-type structure, and the each oxygen atom is surrounded by four Zr atoms [18,19]. On the

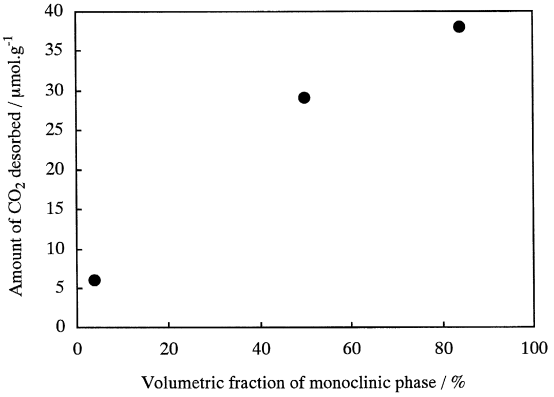

Fig. 4. Relation of amount of CO_2 desorbed from ZrO_2. CO_2-adsorbed at 673 K to volumetric fraction of monoclinic phase in ZrO_2.

other hand, Zr atoms in the monoclinic structure have seven oxygen ions in the coordination sphere [18,19], indicating that Zr atoms in monoclinic phase has one vacant coordination site. As this description is for the bulk of ZrO_2, there should be more vacant sites on the surface because of keeping balance of the charge of ZrO_2. The coordinate unsaturation on the surface of monoclinic structure is higher than that on tetragonal structure. Since there should be two or three vacant sites for the hydrogenation reaction, the faster formation of methoxy and formate species on the monoclinic phase is ascribed to the higher degree of coordinate unsaturation.

Oxygen atoms in tetragonal structure are all surrounded by four Zr atoms, indicating that their coordination spheres are saturated. On the other hand, the configuration around oxygen atoms in monoclinic structure shows that four oxygen atoms in seven are in almost the same configuration as in tetragonal structure but remaining three are surrounded by three Zr atoms [18]. This indicates that three oxygen atoms in seven in monoclinic structure have one uncoordinated electron pair and therefore, are able to adsorb the compounds with Lewis acidity or to abstract proton from acidic compounds.

Thus, the amount of CO_2 adsorbed was measured by TPD method. As shown in Fig. 4, the amount of CO_2 desorbed is correlated with the volumetric fraction of the monoclinic phase. The amount of desorbed CO_2, 38 μmol g^{-1}, with ZrO_2(9.0) is very close to the amount of methoxy species, 35 μmol g^{-1}, on the same catalyst during the CO hydrogenation reaction (Table 3). If 0.51 nm is used for Zr–Zr distance of cubic structure instead of monoclinic for simplicity of estimation [20], there are approximately 4.3×10^{20} of Zr atoms on the surface, where 111 m^2 g^{-1} of ZrO_2 is used as the surface area. Therefore, the amounts of CO_2 desorbed and methoxy species adsorbed are approximately 6% of surface Zr atoms of monoclinic phase, since volumetric fraction of monoclinic phase is 84%. The results that the formation of formate species is parallel to that of methoxy species may suggest that the sites, on which CO_2 strongly adsorbs and methoxy species are present, are all active for the hydrogenation of CO to form methoxy, because it is unlikely that both methoxy and formate species are formed on the very small amount of sites and rapidly transform to the surface of monoclinic phase. However, we have no evidence to clarify whether the conversion of methoxy species to C_2 intermediate, which is the key step in the formation of isobutene from CO and H_2 [10], occurs on the same sites or not.

4. Conclusions

(1) Isobutene is formed from CO and H_2 on the surface of monoclinic phase over ZrO_2, while formation of the other hydrocarbons is independent of the structure of ZrO_2.

(2) The effectiveness of monoclinic structure is attributed to the unsaturation of coordination sites and the strong basicity.

(3) The coordinately unsaturated sites on monoclinic phase are assumed to be effective for the formation of methoxy species.

(4) The strong basicity on monoclinic phase is available for the aldol condensation reaction

to form C_3 hydrocarbons from the C_2 oxygenate and branched C_4 compounds from C_3 oxygenate.

References

[1] H. Pichler, K.H. Ziesecke, Brennst.-Chem. 30 (1949) 13.
[2] E.M. Cohn, in: P.H. Emmett (Ed.), Catalysis vol. 1 Reinhold, New York, 1961, p. 443.
[3] K. Maruya, A. Inaba, T. Maehashi, K. Domen, T. Onishi, J. Chem. Soc., Chem. Commun. (1984) 487.
[4] T. Maehashi, K. Maruya, K. Domen, K. Aika, T. Onishi, Chem. Lett. (1984) 747.
[5] T.J. Mazanec, J. Catal. 98 (1986) 115.
[6] S.C. Tseng, N.B. Jackson, J.G. Ekerdt, J. Catal. 109 (1988) 284.
[7] R.B. Anderson, J. Feldman, H.H. Storch, Ind. Eng. Chem. 44 (1952) 2418.
[8] R. Kieffer, G. Cherry, J. Varela, R. Touroude, J. Chim. Phys. Phys.-Chim. Biol. 84 (1987) 901.
[9] H. Idriss, R. Kieffer, P. Chumette, D. Durand, Ind. Eng. Chem. Res. 30 (1991) 1130.
[10] K. Maruya, A. Takasawa, M. Aikawa, T. Haraoka, K. Domen, T. Onishi, J. Chem. Soc., Faraday Trans. 90 (1994) 911.
[11] K. Maruya, A. Takasawa, T. Haraoka, K. Domen, T. Onishi, J. Mol. Catal. A: Chem. 112 (1996) 143.
[12] M. Ai, Catalysis 12 (1996) 152.
[13] L. Lu, T. Hayakawa, T. Ueda, M. Hara, K. Domen, K. Maruya, Chem. Lett. (1998) 65.
[14] H. Toraya, M. Yoshimura, S. Somiya, Commun. Am. Ceram. Soc. (1984) C-119.
[15] H. Toraya, J. Appl. Crystallogr. 19 (1986) 440.
[16] K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, T. Onishi, Bull. Chem. Soc. Jpn. 61 (1988) 667.
[17] M. Hara, M. Kawamura, K. Maruya, Chem. Lett. (1997) 309.
[18] D.K. Smith, H.W. Newkirk, Acta Crystallogr. 18 (1965) 983.
[19] M. Yashima, T. Hirose, S. Katano, Y. Suzuki, M. Kakihana, M. Yoshimura, Phys. Rev. B 51 (1995) 8018.
[20] D.C. Bradley, P. Thornton, in: J.C. Bailer, H.J. Emeleus, R. Nyholm, A.F. Trotman-Dickson (Eds.), Comprehensive Inorg. Chem. vol. 3 Pergamon, 1973, p. 419.