Correlation Between the Catalytic Property and Zr^{3+} Ion for ZrO$_2$ in F-T Reaction

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Abstract　　CO hydrogenation was studied over zirconia catalysts. The catalysts, which were classed into three types of samples—the fresh, used and specially treated catalysts, were characterized by means of EPR spectroscopy. A strong signal at $g_\perp = 1.976$ and $g_\parallel = 1.961$, which was assigned to Zr^{3+} ion on the surface of ZrO$_2$, was observed for the fresh catalysts. In contrast, unique strong and sharp signal at $g = 2.0024$, which was assigned to dissociated H atom, also was observed for the used catalysts. Further verification of the assignments was carried out by EPR characterization of the specially treated catalysts. These results show that Zr^{3+} ion might involve in CO hydrogenation. Quantitative studies reveal that there is a close linear relation between Zr^{3+} ion and the selectivity to isobutene for the reaction over ZrO$_2$. Finally, a possible mechanism of the catalytic reaction via a surface species $\vdash$Zr(Ⅲ)(CO)$_2$ was proposed.

Keywords: EPR spectra,　ZrO$_2$ catalyst,　Zr^{3+} ion

1　Introduction

Recent studies have showed that ZrO$_2$ catalyst is highly selective for the synthesis of isobutene from CO and H$_2^{[1,2]}$. Hence, it is worth developing the catalyst for syngas to olefins. For isosynthesis feature of ZrO$_2$ catalysts, Jackson[3] suggested a mechanism involving a η^3-enolate intermediate species. According to the mechanism n-C$_4$ and iso-C$_4$ compounds could be formed, but isobutanol, isobutane or isobutene, were not predicted by the mechanism. In our experiments[2], the selectivity of 44% to isobutene was achieved for ZrO$_2$ catalyst but isobutane and isobutanol were not detected at all. The catalytic mechanism of producing isobutene is still an open problem. As a catalyst, the surface ion valence state and the nature of metal oxide play a major role in catalytic properties. Therefore, we attempt to study the metal ion valence state on the surface of ZrO$_2$ and its behavior during the reaction by EPR technique. EPR spectroscopy of ZrO$_2$ has been studied by some authors. Torralvo[4] studied the crystallization behavior of ZrO$_2$ and observed three EPR signals. A strong signal ($g_\perp = 2.012$ and $g_\parallel = 2.004$) was assigned to

F_s^+, the signal ($g_\perp=2.004$ and $g_\parallel=2.002$) observed only during the process of reoxidation was assigned to some kinds of paramagnetic oxygen center, but the weak signal ($g_\perp=1.981$ and $g_\parallel=1.956$) which disappeared while calcination time lengthening was not assigned exactly. Morterra[5] also investigated ZrO_2 by EPR technique and the signal ($g_\perp=1.978$ and $g_\parallel=1.953$) was assigned to Zr^{3+} certainly. At the same time, adsorption of some molecules(e.g. H_2O, CO) was also studied. But a detailed understanding of the origin and reactivity of Zr^{3+} centers is not yet achieved. Although EPR studies of ZrO_2 have been made by the above authors, the system of ZrO_2 as a catalyst for F-T synthesis of olefins has not been examined up to now by EPR technique.

2 Experimental

Zirconia was prepared by the procedures as follows: $Zr(OH)_4$ was precipitated by adding 17 mol·L^{-1} ammonia solution into $ZrCl_4$(purchased from Merck Co. in German) aqueous solution, then the gel was dried at 373K for 15h after filtering and washing the precipitate. The dried sample was calcined at 773K for 3h. EPR spectra of ZrO_2 catalysts were recorded at room temperature by a Varian E-115 spectrometer operating in the x-band. Also some specially treated samples were measured *in situ* by EPR technique. All the catalysts examined were classed as fresh catalysts, used catalysts and specially treated catalysts.

3 Results and Discussion

The typical spectra of two fresh catalyst samples are shown in Fig.1. A strong signal($g_\perp=1.976$ and $g_\parallel=1.961$) was observed at room temperature. This signal is a typical one from d^1 electronic configuration. Asymmetry of the peak and its g value are very similar to those of Ti^{3+} species on $TiO_2^{[6]}$, so the signal was assigned to Zr^{3+} ion on ZrO_2 in accord with Morterra's[5]. But, in Torralvo's work[4], a stronger signal of $g_\perp=2.004$ and $g_\parallel=2.002$ was observed and its intensity rapidly increased with lengthening calcination time at 623K. This difference may be due to the reagents used in the preparation of ZrO_2 because they used zirconium nitrate as the starting material. So, residual ammonium nitrate might exist in the zirconium hydroxide prepared. Therefore, predominant F_s^+ (a single electron trapped in oxygen vacancy) centers were formed due to the microexplosion of NH_4NO_3 while the sample was calcined at 623K. Our experiments have shown that the intensity of the signal assigned to Zr^{3+} ion increases with increasing calcination temperature and lengthening calcination time[7]. In addition, a broad weak EPR signal also was observed for a few samples ($g_\perp=2.021$ and $g_\parallel=2.007$). This signal may be assigned to some kinds of paramagnetic oxygen centers. For all samples measured above, Zr^{3+} species on ZrO_2 is stable at room temperature in air, in other words, it is not easy to reoxidize Zr^{3+} into Zr^{4+} ion. But when pure oxygen gas flowed through ZrO_2 catalyst at 713K for 1h, Zr^{3+} ion was oxidized to Zr^{4+} ion. Fig.2 illustrates the EPR spectra of ZrO_2 catalyst before and after being oxidized by O_2. Hence, Zr^{3+} ion could be reoxidized at the temperature of catalytic reaction.
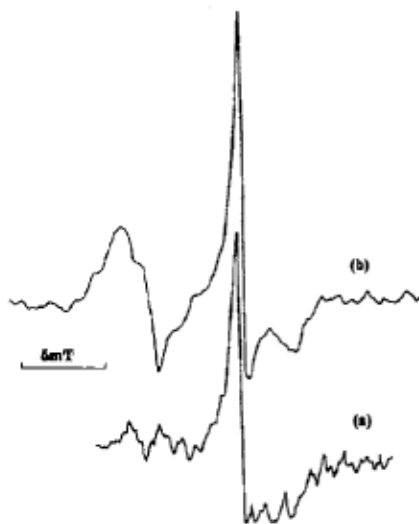
Fig.1 EPR spectra of two fresh ZrO$_2$ catalysts

The used catalysts were also characterized by EPR technique. While a catalyst was being used during the reaction process of CO hydrogenation (10 atm. 1atm=1.01×10^{5}Pa, H$_2$:CO=1:3, at 723K) the reaction was stopped by closing the reaction system. When the system was cooled to room temperature, the used catalyst was taken out from the reactor and was measured by EPR technique. EPR spectra of all catalysts measured showed that only a very narrow and symmetrical signal (g=2.0024) was observed (See Fig.3). This result shows that not only Zr^{3+} ion must take part in the reaction process but also Zr^{3+} ion indeed is on the surface of ZrO$_2$. However, we found out that the product was only methane when the catalytic reaction was carried out under atmosphere pressure at 713K. In this case, the EPR spectrum of the used catalyst was the same as that of the fresh catalyst. This fact might imply that Zr^{3+} species may be the active site of producing isobutene during the catalytic reaction. In order to understand the played role by Zr^{3+} in the reaction process, we carefully chose four catalysts which had closely composition of crystal phases and BET surface areas, as those of the fresh catalysts to be measured by EPR technique. Therefore, although the heterogeneous reaction is complex the results of those four catalysts characterized by estimating the catalytic reaction and EPR spectra would show the role of Zr^{3+} ion during the reaction process. The catalytic reaction was carried out at 723K and under the pressure of 10atm (1atm=1.01×10^{5}Pa, H$_2$/CO=3:1, space velocity 690h^{-1}). The results showed that there is a close linear relation between the concentrations of Zr^{3+} ion on the surface and the selectivity to isobutene for the catalysts, illustrated as Fig.4. Some major data are give in Table 1.

Finally, further EPR measurements of ZrO$_2$ catalysts treated particularly were carried out in order to understand the catalytic mechanism. After the fresh catalyst, of which EPR spectrum is illustrated in Fig.1(a), was reduced for 40 min by flowing H$_2$ at 713K there are two kinds of EPR spectra. If the system was outgassed under vacuum (1Pa) at 713K after the reduction the EPR spectra of the reduced catalysts was the same as that of the fresh catalyst. If not outgassed the signal of g=2.0024 only was observed for the reduced catalysts as illustrated in Fig.3. And also after the similar treatment was done by CO for the fresh catalyst, the signal of $g_\perp$=1.976 and $g_\parallel$=1.961 did not have any change, compared to the fresh catalyst, but a signal attributed to a kind of paramagnetic oxygen center with very low intensity was observed. In the experiment for the sample treated

1076

with CO, the signal ($g=2.0024$) which may be given from C_{ads} *via* Boudouard reaction did not appear at all. Hence, the signal of $g=2.0024$ was finally assinged to the dissociated H species.
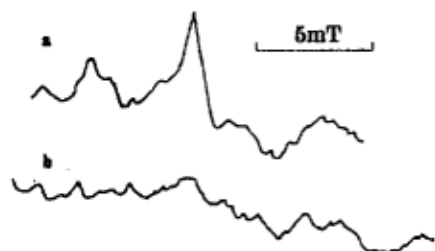
Fig.2 EPR spectra of catalysts (a) the fresh (b) the catalyst oxidized with O_2 at 713K for 1h
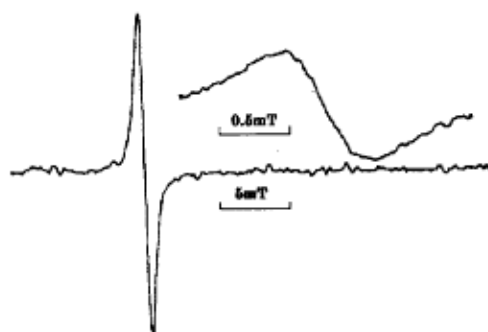
Fig.3 EPR spectrum of the used catalyst (F-T reaction)

Table 1 Some major experimental data

| signal assignment	$g_1 (g_\perp=1.976, g_\parallel=1.961)$ Zr^{3+}	$g_2=2.0024$ H		$g_3(g_\perp=2.021, g_\parallel=2.007)$ oxygen species
I^*	100	66	27	0
S^*	44.8	27.4	5.5	0

*I stands for the relative intensity of g_1 signal ($I=100 I_i/I_0$) and S the selectivity to isobutene
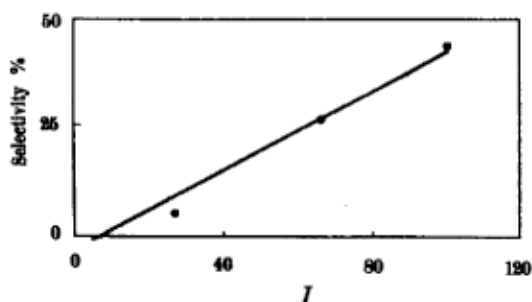
Fig.4 The relation between the selectivity to isobutene and the intensity of the signal ($g_\perp=1.976$ and $g_\parallel=1.961$)

In our previous studies, CO twin adsorption has been recognized by *in situ* FT-IR technique[8]. Theoretical study by quantum calculation method also show that good selectivities to olefins could be obtained for CO hydrogenation on ZrO_2. Especially, the electronic structures of the calculated model molecules support the process of breaking O–C bond of surface species containing ⊢Zr-O-C- fragment, but not that of breaking Zr O bond and forming η^3-enolate[9]. Hence, On the basis of the experimental results, a catalytic mechanism of syngas to isobutene is firstly suggested as follows, at first, under high pressure of syngas CO twin adsorption is formed at Zr^{3+} site on the surface of ZrO_2. This twin adsorption of CO is the species of producing isobutene. Then the species undergo the hydrogenation and chain growing by CO insertion reaction and finally give rise to isobutene.

$$Zr + 2CO \longrightarrow \ \longrightarrow \ \longrightarrow$$

$$\longrightarrow \ \longrightarrow (CH_3)_2CCH_2 + \ \longrightarrow \cdots$$
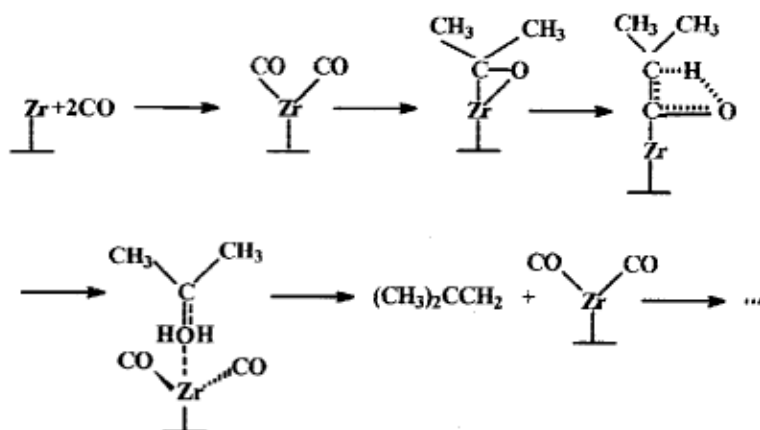
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ZrO₂ 催化剂表面 Zr³⁺ 离子与 F-T 反应中异丁烯选择性的相关性

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摘要 研究了 ZrO₂ 催化剂体系中的 CO 加氢反应, 并对催化剂的使用前后以及特殊处理催化剂进行了 EPR 表征. 在使用前催化剂中观测到了一个较强的 EPR 信号 $g_\perp = 1.976$ 和 $g_\| = 1.961$, 并指认为来自 ZrO₂ 表面的 Zr³⁺ 离子, 而 F-T 反应评价后催化剂均给出了唯一较强和尖锐的信号 $g = 2.0024$ 并指认为来自催化剂表面的解离 H 原子. 通过进一步的 EPR 表征, 结果均显示 Zr³⁺ 离子可能参与了反应过程. 定量研究表明, 催化剂表面 Zr³⁺ 离子浓度与反应中异丁烯的选择性有一近似的线性关系. 最后, 推测了依其表面物种 ⊢Zr(Ⅲ)(CO)₂ 形成异丁烯的可能催化机理.

关键词: EPR, ZrO₂ 催化, Zr³⁺ 离子