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NOTE

Metal–Support Interactions in Fe/ZrO_2 Catalysts for Hydrogenation of CO

Many studies have provided evidence for the existence of strong metal–support interactions (SMSI) between Group VIII metals and various metal oxide supports. Most of the pioneering work was concentrated on TiO_2-supported Group VIII metals (1–4). In the past two decades great attention has been paid to the SMSI effect (5, 6). This high temperature reduction effect not only changes the chemisorption capacity but also changes the reaction activity and selectivity. The hypotheses attempting to explain this phenomenon can be put into three categories (7): (I) an energetic effect, (II) an electronic effect, and (III) a geometric effect. Some examples of these effects follow, but clearly more than one of them may be acting simultaneously in certain cases. Titania is not the only support to show the SMSI effect. Oxides of zirconium, vanadium, manganese, and niobium are also reported to exhibit the SMSI effect (8, 9).

Zirconia is currently attracting considerable scientific interest for its potential use as a catalyst support or promoter for a variety of catalyst systems (10, 11). Turlier and Martin (12) studied the SMSI effect of Ni/ZrO_2 catalyst for ethane hydrogenolysis. Recently, we reported (13) on Fe/ZrO_2 catalysts which exhibited high olefin selectivity for hydrogenation of CO. The present study has been undertaken to probe the nature of metal–support interactions between iron and zirconia.

Fe_2O_3/ZrO_2 catalyst with 7 wt.% Fe_2O_3 loading was prepared by the impregnation method. Zirconia powder (ca. 100 mesh, surface area 39 m^2/g, Shanghai) was impregnated with an aqueous solution of iron nitrate and then dried at 393 K for 12 h and calcined at 773 K for 5 h. Before various catalyst characterization and CO hydrogenation tests, the sample was reduced in pure hydrogen at 573 K for 10 h, 673 K for 2 h, 773 K for 2 h, and in 5.6% (vol/vol) H_2/Ar mixture at 973 K for 0.1 h. Since a long reduction time in pure hydrogen at very high temperature would have caused serious sintering or agglomeration of the catalyst, the sample was reduced at 973 K in 5.6% H_2 and Ar mixture for only a few minutes. A CO hydrogenation reaction test was carried out in a U-type quartz fixed bed microreactor and the catalytic properties were determined after the reaction reached steady state (ca. 6 h) with the reaction conditions at 643 K, 1 atm, $H_2/CO = 1.7$ (vol/vol), and gas hour space velocity (GHSV) ca. 700 h^{-1}. Reaction products were analyzed by an on-line gas chromatograph equipped with a Porapak-QS column and a thermal conductivity detector. Mössbauer spectroscopy and XPS were performed at room temperature as described in Ref. 13. BET surface area measurement was carried out on a Micromeritics ASAP 2000 instrument (N_2 adsorption at 77 K). H_2 chemisorption was measured in a U-type quartz microreactor by the desorption method as described in Ref. 14. The sample was first reduced under various conditions (as described above) and cooled to room temperature in the same atmosphere; the reactor was then purged with Ar for 20 min for removal of the physisorbed gas. H_2 desorption was then conducted in an Ar flow with a heating rate of 16 K/min and monitored by a thermal conductivity detector. CO-TPD was performed in the same U-type quartz microreactor. The reduced sample (as described above) was first purged with Ar for 1 h at 773 K and then cooled to room temperature. The adsorption of CO was conducted by passing a flow of CO through the sample for 0.5 h at room temperature and purging with Ar for 20 min to remove physisorbed gas. CO desorption was then carried out in an Ar flow with a heating rate of 16 K/min and was monitored by a thermal conductivity detector. The flow rates used in reduction, outgassing, adsoption and desorption were, in all cases, 30 ml/min.

Table 1 shows the catalytic activity and selectivity of Fe/ZrO_2 catalysts pretreated in various conditions. It is shown that CO conversion decreases with increasing reduction temperature, while the olefin/paraffin ratio increases. For the catalyst reduced in 5.6% H_2 and Ar mixture at 973 K, no hydrocarbon product was detected. This indicates that an increase in reduction temperature poisons hydrogenation activity and inhibits carbon chain polymerization. The H_2 chemisorption result is shown in Table 2. It can be seen that less H_2 is chemisorbed by the high temperature reduced sample compared with that of the low temperature reduced one. For the sample reduced at 973 K, hydrogen chemisorption is seriously suppressed and falls nearly to zero. The above results all suggest that the number of active sites for H_2 chemisorption and CO hydrogenation has significantly decreased after high temperature reduction. Because the BET surface area of the Fe/ZrO_2 catalysts reduced below 773 K does not significantly change (see Table 2), the decrease of the active site number with increase of the reduction temperature cannot result from the

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TABLE 1

CO Hydrogenation on Fe/ZrO_2 Catalysts Reduced under Various Conditions

Treatment condition	CO conversion (%)	Hydrocarbon distribution (%wt)				
		C_1	C_2	C_3	C_4	$C_{2-4}^{=}/C_{2-4}$ (%)
H_2, 573 K, 10 h	4.9	33.8	31.3	26.6	8.3	76.4
H_2, 673 K, 2 h	1.8	32.5	30.3	25.8	11.4	81.6
H_2, 773 K, 2 h	0.8	77.5	12.2	10.3	—	100.0
5.6% H_2/Ar, 973 K, 0.1 h	≈0.0	No hydrocarbons formed				

sintering of the catalyst. From Table 3 it is shown that for the samples reduced below 773 K, the proportion of bulk phase Fe^0 increases with the increase of reduction temperature, and the metallic iron carburizes and transforms to χ-Fe_5C_2 after reaction in syngas. Since the proportion of bulk phase Fe^0 increases after higher temperature reduction, we can conclude that the decrease of the active site number for H_2 chemisorption and CO hydrogenation must have originated from a decrease of the number of exposed surface metallic iron atoms. The metallic iron surface might have been decorated by small zirconia particles after high temperature reduction. This assumption is supported by XPS results (see Table 2). For the samples reduced below 773 K, the surface Fe/Zr atomic ratio decreases with increasing the reduction temperature, suggesting a covering by zirconia species of the surface of the metallic iron particles. For the very high temperature (973 K) reduced sample, the proportion of metallic iron is a little lower than that of the sample reduced in pure hydrogen at 773 K. This may be caused by the short reduction time and the low H_2 concentration during the reduction course. For this sample, it is surprising to find that it has lost its H_2 chemisorption property and catalytic activity for CO hydrogenation, and the metallic iron cannot carburize after reaction in syngas. These phenomena also strongly suggest that the metallic iron surface of the Fe/ZrO_2 catalyst must have been almost totally covered by zirconia species after the very high temperature reduction.

The above results all suggest that migration of small zirconia particles onto the top of the metallic iron surface must have occurred during the course of reduction. Similar results have been obtained in Fe/TiO_2 (14–16) and Fe/C (17, 18) systems. Figure 1 shows the surface model of Fe/ZrO_2 catalysts after reduction in various conditions. With the reduction temperature increasing from 573 to 973 K, the mobility of the surface zirconia in the vicinity of the metal–support interfaces is enhanced, and more and more zirconia species migrate onto the surface of the metallic iron. These small zirconia islands cover part of the metallic iron surface and block some active sites for H_2 adsorption and CO hydrogenation and dramatically decrease the number of active sites. This results in the decrease of H_2 chemisorption and CO conversion. The very high methane selectivity for the 773 K reduced catalyst can also be interpreted by the decoration of small zirconia particles on the metallic iron surface, owing to the possibility of carbon chain growth on the metallic iron surface (which is significantly covered and isolated by zirconia particles) being strongly restricted. Similar results have been obtained by Santos *et al.* (15) and Tau *et al.* (14) in the Fe/TiO_2 system.

TABLE 2

H_2 Chemisorption, BET Surface Area and Surface Fe/Zr Ratio of Fe/ZrO_2 Catalysts Treated under Various Conditions

Treatment condition	H_2, 573 K, 10 h	H_2, 673 K, 2 h	H_2, 773 K, 2 h	5.6% H_2/Ar, 973 K, 0.1 h
H_2 uptake (μmol/g · cat.)	99.3	93.0	62.6	≈0.0
S_{BET} (m^2/g)	30.1	30.3	29.8	16.4
Fe/Zr	0.26	0.17	0.11	0.33

TABLE 3

Iron Species of Fe/ZrO_2 Catalysts Treated under Various Conditions

Treatment condition	Iron species (%)		
	Fe_2O_3	α-Fe	χ-Fe_5C_2
H_2, 573 K, 10 h (A)	34	66	0
H_2, 573 K, 10 h (B)	37	0	63
H_2, 673 K, 2 h (A)	23	77	0
H_2, 673 K, 2 h (B)	25	0	75
H_2, 773 K, 2 h (A)	13	87	0
H_2, 773 K, 2 h (B)	10	0	90
5.6% H_2/Ar, (A) 973 K, 0.1 h	28	72	0
5.6% H_2/Ar, (B) (973 K, 0.1 h	28	72	0

Note. A, as-reduced sample; B, after reaction in syngas for 6 h.

It is pertinent to note that the surface Tammann temperature of zirconia is 891 K. For the H_2/Ar mixture 973 K reduced catalyst, on the one hand, the low H_2 concentration and very short reduction time result in only a very small amount of zirconia migrating onto the surface of metallic iron during the course of reduction; hence the surface Fe/Zr atomic ratio measured by XPS may be larger than that of the samples reduced in pure hydrogen below 773 K for a rather long time. On the other hand, the reduction temperature is much higher than the surface Tammann temperature of zirconia; therefore, under the reduction conditions, the small zirconia particles on top of the metallic iron and in the vicinity of the metal–support interface can have sufficient mobility to spread over the entire iron surface and cover it as a very thin layer. This leads to only a few metallic iron atoms being left exposed on the surface of the catalyst.

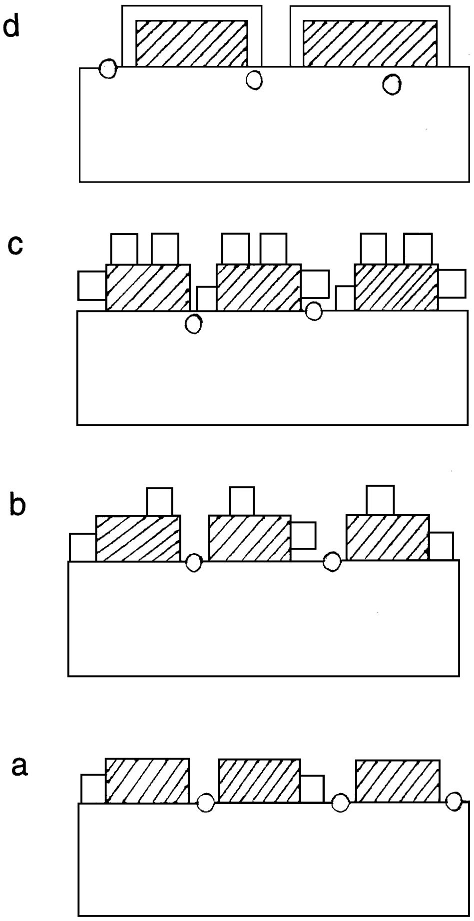

FIG. 1. Surface model of Fe/ZrO_2 catalyst treated under various conditions: (a) H_2, 573 K, 10 h; (b) H_2, 673 K, 2 h; (c) H_2, 773 K, 2 h; (d) 5.6% H_2/Ar, 973 K, 0.1 h. ▭, Zirconia support; ▨, metallic iron particles; □, small zirconia particles; ▭, zirconia thin layer on the surface of metallic iron particles; ○, Fe^{3+} cations doped in zirconia support.

Hence the H_2 chemisorption and the catalytic activity are seriously suppressed, and the metallic iron cannot be carburized.

CO-TPD was used to study the surface electronic state of Fe/ZrO_2 catalysts reduced in various conditions. It was found that the desorption peak maximum of CO shifts from 673 to 693 K with the reduction temperature increasing from 673 to 773 K, indicating an enhancing of the Fe–C bond strength after high temperature reduction. In other words, the electron backdonation from the metal into the $2\pi^*$ orbital of CO increases. This suggests that the surface electron density of the metallic iron increases after the sample is treated at 773 K. The increase of the olefin selectivity in C_2–C_4 hydrocarbons after high temperature reduction also supports this view (19). For the Fe/ZrO_2 system, it has been shown (13) that the surface ZrO_2 can be partially reduced to electron-rich ZrO_x ($1.5 < x < 2$) during the high temperature ($\geq$773 K) reduction. Hence we propose that electrons might transfer from the partially reduced ZrO_x to the metallic iron surface during the course of high temperature reduction. A similar conclusion has been drawn by Yoshitake and Iwasawa (20) for the Pt/ZrO_2 system.

In short, it can be suggested from the above discussion that a strong metal–support interaction exists in the Fe/ZrO_2 system and that this SMSI effect results from the migration and covering of partially reduced zirconia species on the surface of metallic iron particles during the high temperature ($\geq$773 K) reduction.

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