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Surface coordinate geometry of iron catalysts: hydrogenation of CO_2 over Fe/ZrO_2 prepared by a novel method

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Zirconia-supported iron oxide catalyst has been designed following the approach to the Fe/TiO_2 catalyst. The catalyst prepared by reducing the precursor obtained from incipient wetness impregnation in H_2 at the proper temperature exhibits good activity (CO_2 conversion $> 20\%$) and selectivity (68%) in the selective synthesis of hydrocarbons (C_2–C_5) from CO_2 and H_2. The catalytic activity has been found to vary with iron weight loadings in a "two maxima" fashion and is also affected by reduction temperature. Mössbauer and EXAFS analyses suggest that the active phases are coordinatively unsaturated ferric cations and α-Fe. No ferrous cations are observed. A good geometric arrangement for the two phases on the catalyst is thought to give the highest catalytic activity.

Keywords: iron catalyst; zirconia; hydrogenation of CO_2; Mössbauer; EXAFS

Supported iron oxide catalysts are well known for the hydrogenation of CO but studies of the catalyst for hydrogenation of CO_2 are rare [1–3]. Interactions of iron oxides with metal oxide supports have been extensively studied [4–8], and the influence of geometric tendencies of iron cations and supports on the formation of either a structurally stable interface or a catalytically active surface have been particularly emphasized in the present series [1,9–12]. In order to avoid the formation of geometrically stable iron oxide ensembles on the surface a novel preparation has been developed. The Fe/TiO_2 so prepared exhibits good activity (CO_2 conversion $> 24\%$) and selectivity ($> 60\%$) in the selective synthesis of hydrocarbons from CO_2 and H_2 [1]. Questions arising therefrom are whether the preparation is

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effective when other supports are used and what makes the Fe/TiO_2 so different from the well-defined $Fe(III)/TiO_2$ [9]. The present work is aimed at providing further evidence by using zirconia as support. Zirconia is different from titania in many ways. Based on geometric consideration, i.e., reducing the structural similarities between iron oxide and the support as much as possible, it is most important for the present studies that zirconia tends to have unusual structures. Four forms of zirconia have been described but none has the rutile structure so often found among MO_2 compounds such as TiO_2. In fact, zirconia in its monoclinic form has a very unique, seven-coordinate structure. Zirconia as a support is not easily reducible and is very stable to high temperature. Thus, in a practical sense, zirconia may be more suitable for use as an industrial catalyst.

ZrO_2 was obtained from decomposition of $Zr(OH)_4$ at 873 K for 5 h. The powder was pressed into small bars, crushed and sized to 30–60 mesh. The BET surface area was 27 m^2/g. X-ray diffraction (XRD) analysis revealed that the ZrO_2 obtained was dominated by the monoclinic phase. The Fe/ZrO_2 with various iron loadings were prepared by incipient wetness impregnation of the ZrO_2 with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The precursors obtained from the impregnation were dried carefully and then reduced in the reactor at proper temperatures indicated below. The BET surface area of the Fe/ZrO_2 catalyst after use was found to increase to 30–40 m^2/g. Hydrogenation of CO_2 was carried out in a stainless steel reactor (8 mm in diameter) with an on-line GC analyzer under the conditions: 1.5 MPa syngas ($CO_2 : H_2 = 1 : 2$), 623–773 K and GHSV = 800–1000 h^{-1}. XRD experiments were performed on a Rigaku D/Max Diffractometer using Cu K_α radiation. X-ray absorption spectra were obtained using the BL-7C facilities at the Photon Factory (Tsukuba, Japan). A general procedure for the EXAFS (extended X-ray absorption fine structure) data collection and analysis has been given previously [11,12]. Mössbauer spectra were collected using an MR-351 spectrometer. The source consisted of 10 mCi of ^{57}Co diffused into a rhodium matrix. The samples for spectroscopic studies were sealed in flasks under N_2. Specimens were made by directly applying the powders to Scotch tape inside a glove box kept under a N_2 atmosphere, sealed by the tape, and then measured at room temperature immediately.

The Fe/ZrO_2 showed a good activity in catalytic synthesis of lower hydrocarbons (C_2–C_5) from CO_2 and H_2. Over a 5 wt% catalyst, the CO_2 conversion was 17.1% and the selectivity to lower hydrocarbons was 38.3%. Judged by the highest conversion the catalytic activity was found to vary with the iron weight loadings. It can be seen from fig. 1 that the first highest CO_2 conversion is observed when iron loading was 5 wt%, and then, through the lowest point at 6.5 wt%, the conversion exceeded the first maximum immediately and reached a stable level in the range of 10–16 wt%. The second highest conversion appeared at 15 wt%. The best results represented by the catalyst with an iron loading of 15 wt% are: conversion of CO_2 was 20.3% and the selectivity to lower hydrocarbons was 68.6%.

The highest conversion of CO_2 over the Fe/ZrO_2 catalyst is also affected by

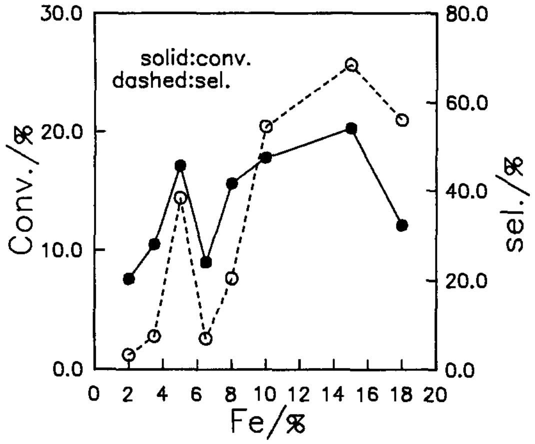

Fig. 1. Relation of the iron weight loadings of the Fe/ZrO_2 with the conversions of CO_2 and the selectivities to lower hydrocarbons (C_2–C_5).

reduction temperature. It can be seen from fig. 2 that the conversion (and the selectivity) increases rapidly by raising the reduction temperature from 673 to 723 K, then decreases gradually from 723 to 823 K. The appropriate reducing temperature for the Fe/ZrO_2 is 723 K, 50 K lower than that for the Fe/TiO_2.

Room temperature Mössbauer spectra collected for the catalysts (5 wt%) prepared by reducing the precursor at 673, 723, and 773 K are shown in fig. 3, and the spectral parameters determined by fitting the data are tabulated in table 1. Unlike those of Fe/TiO_2, the spectra of the Fe/ZrO_2 are very simple and exhibit no significant spectral change while the reduction temperature increases. A sharp doublet

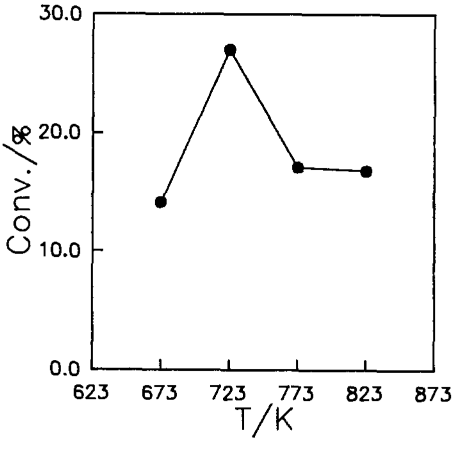

Fig. 2. Relationship between the pre-reduction temperatures and the CO_2 conversions of the Fe/ZrO_2.

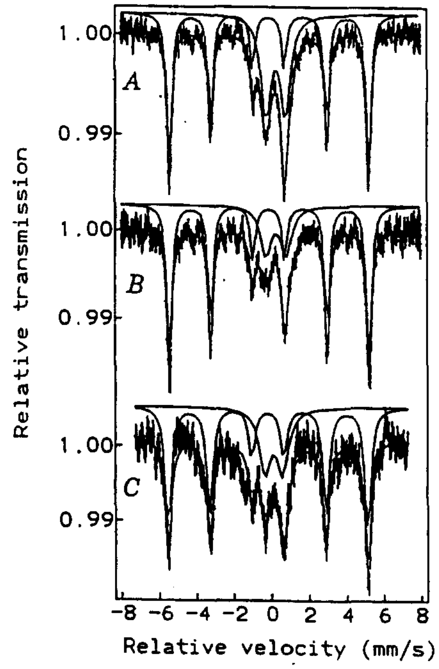

Fig. 3. Mössbauer spectra of the Fe/ZrO_2 pre-reduced at (A) 673 K; (B) 723 K and (C) 773 K.

with an isomer shift (IS) of 0.33–0.38 mm/s and quadrupole splitting (QS) of 0.92–1.06 mm/s is indicative of ferric cations, and the sextuplet is due to zerovalent α-Fe [6,13]. Besides the Fe^{3+} and α-Fe, no Fe^{2+} and superparamagnetic Fe(0) observed for the Fe/TiO_2 is seen. The good relationship between the spectral area of α-Fe and the conversion of CO_2 seems to imply that the α-Fe phase plays a key

Table 1
Mössbauer spectroscopy parameters of Fe/ZrO_2 (5 wt%) catalysts of which the precursors were on-line reduced in the reactor in H_2 at different temperatures [a]

Reduction conditions	Species	IS (mm/s)	QS (mm/s)	H (kOe)	Area (%)
673 K in H_2	α-Fe	0.00	0.00	331.6	61.9
	Fe^{3+}	0.38	1.02		38.1
723 K in H_2	α-Fe	0.00	0.00	332.5	76.2
	Fe^{3+}	0.38	1.06		23.8
773 K in H_2	α-Fe	0.00	0.00	332.1	71.8
	Fe^{3+}	0.33	0.92		28.2

[a] IS = isomer shift relative to metallic Fe; QS = quadrupole splitting; H = hyperfine magnetic field.

role for the high performance of the Fe/ZrO_2 in the hydrogenation of CO_2. In comparison with the Fe/TiO_2, the influence of the support properties on the iron phases formed is very interesting. On the surface of an easily reducible support like TiO_2, ferrous cations and superparamagnetic Fe(0) are observed, but on the surface of ZrO_2, which cannot be reduced easily and has no true hydroxide group, both disappear completely. It is likely that the highest catalytic conversion is achieved by a perfect combination of α-Fe and iron cations, which are Fe^{3+} for Fe/ZrO_2, but are Fe^{2+} for Fe/TiO_2.

Fe K-edge EXAFS-derived Fourier transforms, shown in fig. 4, indicate that the catalysts pretreated at 673, 723 and 773 K have much the same spectral features. The best fits (fig. 5, R-factor = 0.06) to the Fourier transform and the Fourier-filtered EXAFS of the Fe/ZrO_2 (5 wt%) pretreated at an appropriate temperature of 723 K result in 4.0 (±0.09) nearest oxygen neighbors at 2.06± 0.02 Å, 3.5 (±0.4) nearest irons at 2.48 ± 0.01 Å, and 7 (±1.5) next nearest irons at 2.76 ± 0.01 Å. It means that at least about 40% irons on the Fe/ZrO_2 are zerovalent irons and the others are cations. Otherwise, on well-defined Fe/ZrO_2 [9], there were 6.9 nearest oxygens at 2.05 Å and 1.8 nearest irons at a distance as far as 2.86 Å. No Fe–Fe shell at 2.48 Å was found. The present EXAFS-derived data is therefore in good agreement with the Mössbauer results and suggests the formation of α-Fe. In comparison with the well-defined one, the significantly reduced coordination number of the first Fe–O shell is expected, but it is still difficult to understand why the average Fe–O bond length remains similar. The lower coordination number of the Fe–O shell may arise from the formation of metallic irons as well as the formation of coordinatively unsaturated cations. The latter is important for the high activity achieved by the Fe/ZrO_2.

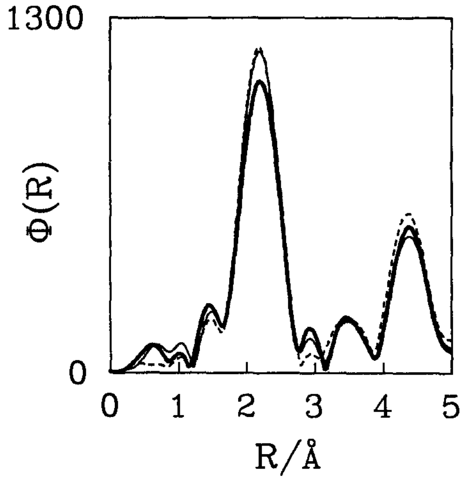

Fig. 4. The Fourier transforms of the Fe/ZrO_2 pre-reduced at 673 K (dashed line), 723 K (solid line) and 773 K (bold line).

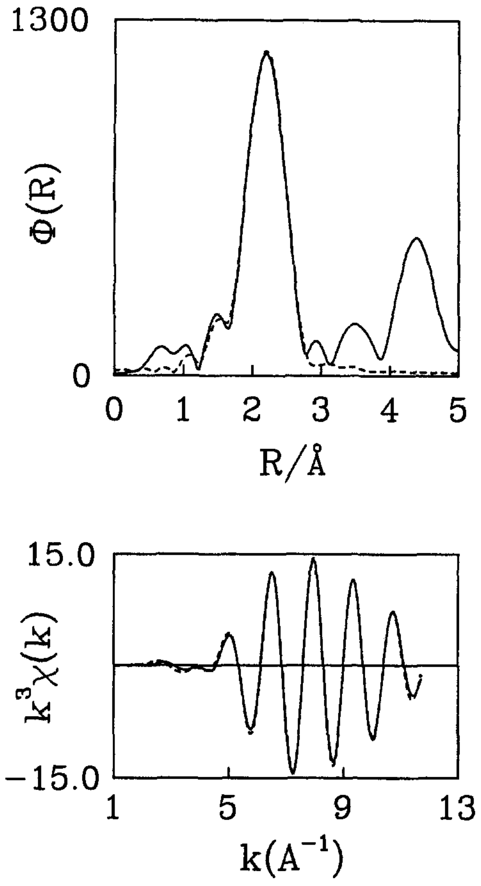

Fig. 5. The best fits to Fe K-edge Fourier-filtered EXAFS and the Fourier transform of the Fe/ZrO_2 pre-reduced at an appropriate temperature of 723 K.

In conclusion, the Fe/ZrO_2 as described exhibits a good catalytic activity in the selective synthesis of hydrocarbons from CO_2 and H_2. Judged by the highest conversion of CO_2, the activity varies with the iron weight loadings and is affected by the reduction temperature of the precursor. The active phases suggested by the Mössbauer and EXAFS results are a combination of α-Fe and coordinatively unsaturated ferric cations. A good geometric arrangement for the two phases is suggested to achieve the highest catalytic level.

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