Surface coordinate geometry of iron catalysts: hydrogenation of CO_2 over Fe/TiO_2 prepared by a novel method

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Received 5 June 1995; accepted 10 September 1995

Titania-supported iron oxide catalyst has been designed based on a geometric consideration. The catalyst prepared by reducing the precursor obtained from incipient wetness impregnation in H_2 at proper temperature exhibits good activity (CO_2 conversion >24%) and selectivity (>60%) 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 "twin maxima" fashion and, also, to be affected by the reduction temperature. Mössbauer and EXAFS analyses suggest that the active phase is coordinatively unsaturated ferrous cations associated with α-Fe. Alternative arrangement of the two phases in a proper way is beneficial to relax the Fe–O bonds and results in the highest catalytic activity for the catalyst, but the formation of predominantly $FeTiO_3$ phase finally makes the catalyst inactive.

Keywords: iron catalyst; titania; hydrogenation of CO_2; Mössbauer; EXAFS; Raman

Well-defined alumina-supported iron oxides as typical examples have depicted the influence of surface coordinate geometry on their catalytic properties in detail [1–3]. An average Fe–O bond length of 1.97 Å is generally observed. The distance between two adjacent oxygens on the surface of γ-Al_2O_3 is 2.80–2.85 Å [4,5]. Thus, when an iron cation is deposited onto the position coordinated with three oxygens on the γ-alumina surface, the iron is, in fact, being centered into a potentially six-coordinate, octahedral site, as shown in fig. 1. If the iron cations are then covered by adventitious oxygens through calcination, the formation of geometrically stable iron oxide ensembles is easy and reasonable. This finding is in full agreement with

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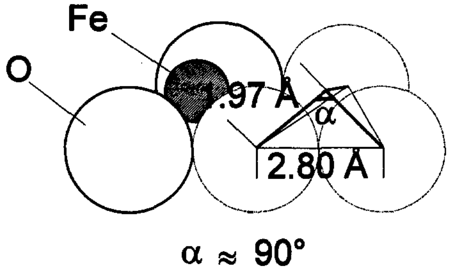

Fig. 1. Geometry of an iron cation deposited onto the triply bridged site of the γ-Al_2O_3(111) face.

the fact that alumina-supported iron oxides are difficult to be reduced even in flowing H_2 at 773 K and that no catalytic activities for CO and CO_2 hydrogenation are found over the catalysts prepared in such a way. It suggests that, in order to promote the formation of structurally unusual iron sites on the surface, direct calcination following the impregnation must be avoided. On the other hand, since the structural similarity between iron oxide and γ-alumina is beneficial to form a geometrically stable phase at the interface, use of a support with unusual structure, less similar to those of iron oxides, is therefore suggested. In this paper, we present the catalytic properties and the Raman and Mössbauer studies of Fe/TiO_2 systems prepared by reducing the precursor obtained from incipient wetness impregnation in flowing H_2 at proper temperatures. The surface structure of the catalyst is then compared with that of well-defined iron oxides using Fe K-edge EXAFS (extended X-ray absorption fine structure).

TiO_2 was prepared by precipitation and hydrolysis of Ti(*i*-OBt)$_4$. The white precipitates were dried at 393 K after filtering, then calcined at 873 K for 5 h. The powder was pressed into small bars and crushed to particles of 30–60 mesh. The BET surface was 20 m^2/g. X-ray diffraction (XRD) analysis revealed 85% anatase and 15% rutile for the TiO_2 obtained. The Fe/TiO_2 with various iron loadings were prepared by incipient wetness impregnation of TiO_2 with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The precursors obtained from the impregnation were dried carefully and then on-line reduced in the reactor at proper temperatures. Hydrogenation of CO_2 was carried out in a stainless steel reactor with an on-line GC analyzer under the conditions: 1.5 MPa syngas ($CO_2 : H_2 = 1 : 2$), 623 K and GHSV = 800–1000 h^{-1}. XRD experiments were performed on a Rigaku D/Max diffractometer using Cu K_α radiation. Raman spectra were collected by using a Spex model 1403 spectrometer. X-ray absorption spectra were obtained using the BL-7C facilities at the Photon Factory (Tsukuba, Japan). A general procedure for the EXAFS analysis has been given by previously published work [6,7]. Mössbauer spectra were collected by using a 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 the protection of N_2. Specimens were made by directly applying the powders to Scotch tape inside a glove box kept under an atmosphere of N_2, sealed by the tape, and then measured at room temperature immediately.

The Fe/TiO_2 shows 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 19.1% and the selectivity to lower hydrocarbons was 50.1% including 2.4% olefins. The other products were 25.1% CO and 24.8% CH_4. Judged by the highest conversion, the catalytic activity is found to vary with the iron weight loadings. It can be seen from fig. 2 that the first highest CO_2 conversion is observed when iron loading is 5 wt%, and then, above the lowest point at 8 wt%, the conversion goes up progressively and exceeds the first maximum when the iron loading reaches 18 wt%. Although the sample with an iron loading higher than 18 wt% was not available from the same preparation procedure because of technical limitations of the incipient wetness impregnation, fig. 2 predicts the second highest conversion near or above 18 wt%. For example, in the case of Fe/ZrO_2 prepared by the same method, the first maximum appeared at 5 wt%, and then, through the lowest point at 6.5 wt%, the second maximum was clearly observed at 15 wt% [3]. The best results represented by the Fe/TiO_2 with an iron loading of 18 wt% were: conversion of CO_2 24.3% and the selectivity to lower hydrocarbons 65.6% (5.7% olefins). The other products were 20.1% CO and 14.3% CH_4. In fact, the higher the conversion reached, the more lower hydrocarbons were obtained, and the less CO. For example, an 8 wt% catalyst (CO_2 conversion: 6.1%) gave 21.5% hydrocarbons but 63.4% CO and 15.1% CH_4. It is likely that, during the reactions, the CO_2 is converted probably through a preliminary water–gas shift reaction to form CO and H_2O and it is the CO and H_2 that react via a Fischer–Tropsch process to form hydrocarbons.

The highest conversion of CO_2 is also affected by reduction temperature. It can be seen from fig. 3 that the conversion (and the selectivity) increases gradually by raising the reduction temperature from 673 to 773 K in 50 K steps, then decreases

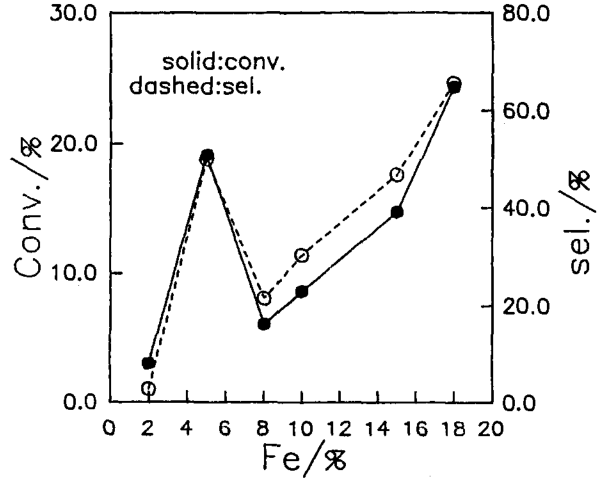

Fig. 2. Relation of the iron weight loadings of the Fe/TiO_2 with the conversions of CO_2 and the selectivities to lower hydrocarbons (C_2–C_5).

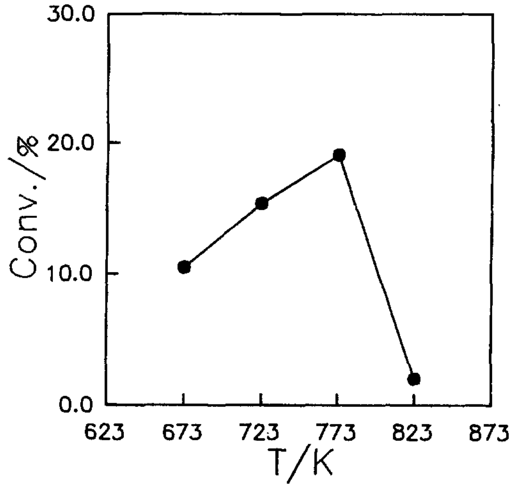

Fig. 3. Relationship between the pre-reduction temperatures and the CO_2 conversions of the Fe/TiO_2.

abruptly from 773 to 823 K. In comparison with the free TiO_2, Raman spectra shown in fig. 4 reveal that the characteristic peaks of Ti–O bonds still remain when the precursor is reduced at 773 K but completely disappear after reduction at 823 K.

Room temperature Mössbauer spectra collected for the catalysts (5 wt%) prepared by reducing the precursor at 723, 773, and 823 K are shown in fig. 5, and the spectral parameters determined by the best fitting are tabulated in table 1. Two sharp doublets are observed in fig. 5A. The doublet A with an isomer shift (IS) of

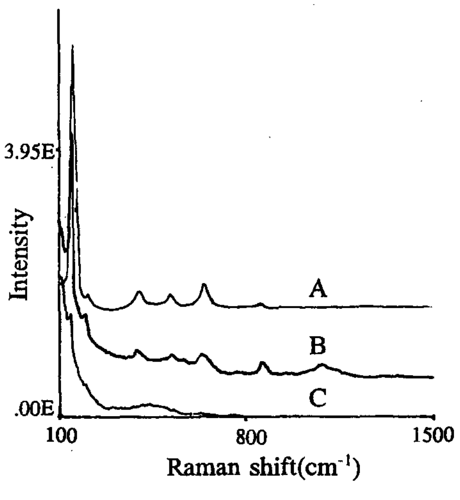

Fig. 4. Raman spectra of (A) the TiO_2 reduced at 773 K; (B) the Fe/TiO_2 pre-reduced at 773 K, and (C) the Fe/TiO_2 pre-reduced at 823 K.

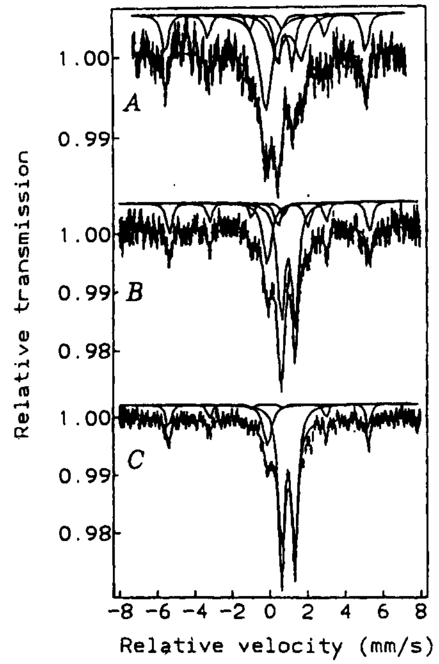

Fig. 5. Mössbauer spectra of the Fe/TiO_2 pre-reduced at (A) 723 K; (B) 773 K and (C) 823 K.

1.08 mm/s and quadrupole splitting (QS) of 0.76 mm/s is indicative of ferrous cations (Fe^{2+}-A) in $FeTiO_3$ [8,9], and the doublet B with a relatively very large IS of 1.30 mm/s and QS of 1.25 mm/s is tentatively assigned to ferrous cations

Table 1
Mössbauer spectroscopy parameters of Fe/TiO_2 (5 wt%) catalysts of which the precursors were on-line reduced in the reactor in H_2 at different temperatures [a]

Reduction condition	Species	IS (mm/s)	QS (mm/s)	*H* (kOe)	Area (%)
723 K in H_2	Fe(0)	0.07			31.7
	α-Fe	0.04	−0.04	332.8	25.5
	Fe^{2+}-A	1.08	0.76		16.4
	Fe^{2+}-B	1.30	1.25		26.4
773 K in H_2	Fe(0)	0.02			17.4
	α-Fe	0.05	0.02	332.5	22.9
	Fe^{2+}-A	1.10	0.73		49.6
	Fe^{2+}-B	1.36	1.57		10.1
823 K in H_2	Fe(0)	0.02			14.2
	α-Fe	0.00	0.02	332.0	16.1
	Fe^{2+}-A	1.09	0.70		69.7

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

(Fe^{2+}-B) in a distorted octahedral site-symmetry. The singlet is caused by superparamagnetic Fe(0) particles and the sextuplet is due to zerovalent α-Fe [8,9]. It is noteworthy that the spectral features observed in fig. 5A completely remain in fig. 5B but are significantly changed in fig. 5C. In fig. 5C, no doublet B can be found. Besides the Fe(0) and α-Fe, only the Fe^{2+}-A in $FeTiO_3$ are seen. The fact that doublet B was also not observed for conventionally prepared Fe/TiO_2 [8] seems to indicate that the cations Fe^{2+}-B having IS = 1.30–1.36 mm/s and QS = 1.25–1.57 mm/s play a key role in the high performance of Fe/TiO_2 in the hydrogenation of CO_2. In comparison with conventionally prepared titania-supported iron oxide, the presence of α-Fe phase is also very interesting. The present results are not sufficient to judge whether or not the α-Fe will play an important role, but based on the changes in spectral area, it is likely that the highest catalytic conversion is geometrically achieved by a proper ratio of Fe^{2+}-B to α-Fe. Concerning the relative spectral area of the components shown in table 1, it can be found that the catalyst reduced at 723 K has much the same features as that reduced at 773 K. Why isn't the Fe/TiO_2 reduced at 723 K the most active catalyst? Knowledge of the surface structures of the catalysts in that case is important. EXAFS studies are therefore performed on both well-defined Fe_2O_3/TiO_2 and Fe/TiO_2 for the purpose of determining the site-geometries of irons.

In order to describe the interface between the supported iron oxides and the substrate TiO_2 as well as to understand how significant the difference will be between the TiO_2 used and crystalline titanias, Fe K-edge EXAFS of well-defined Fe_2O_3/Al_2O_3 is comparatively studied with Ti K-edge EXAFS of the TiO_2. EXAFS-derived Fourier transforms shown in fig. 6 indicate that, following the most intense peak contributed by the nearest oxygen neighbors, both of them show three well-resolved peaks in the range of 2–5 Å. It seems that the structure of the iron cation on the surface of Fe_2O_3/TiO_2 is somewhat similar to and/or significantly influenced by the lattices of the TiO_2.

The best fits to the Fourier-filtered EXAFS of the TiO_2 and to that of the Fe_2O_3/TiO_2 are summarized in fig. 6 and table 2. The structural unit in crystalline anatase and rutile is a TiO_6 octahedron. The Ti–O bond length is about 1.95–1.96 Å [10]. However, for the TiO_2 practically used as a support, mixing of the rutile units into the predominant anatase phase as suggested by XRD may result in a significant distortion of the lattices and different stacking of those octahedra. Much more, it is known that the lattices contain a large number of both cation and anion vacancies. It is therefore not surprising that the Ti sites in the TiO_2 used in this work are less similar to either crystalline rutile or anatase. It can be seen from the first two shells listed in table 2 that there are 7.3 nearest oxygens at an average distance of 1.975 ± 0.007 Å. I comparison with the XRD results, the increase in the coordination number (CN) of the nearest oxygens does not mean that the local geometry of the Ti sites but the long-range-ordered feature expected for the crystalline TiO_2 is significantly changed via the distortion and the different stacking. Furthermore, the second nearest oxygens at 2.71 ± 0.03 Å with a CN as high as 3.5

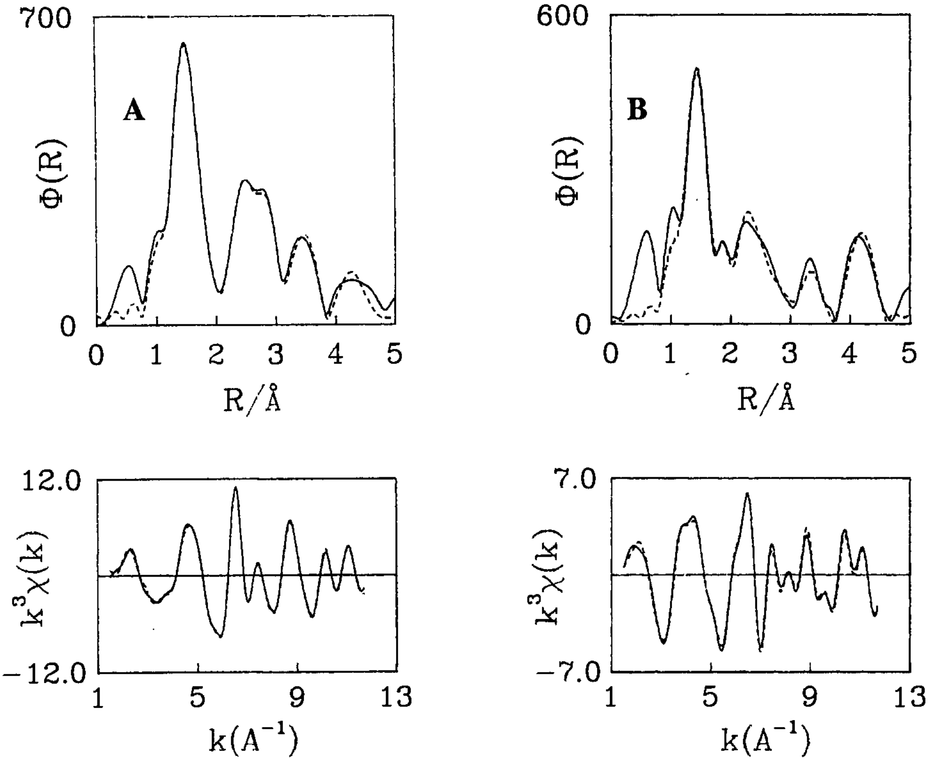

Fig. 6. The best fits (dashed line) to (A) Ti K-edge Fourier-filtered EXAFS and the Fourier transform of the TiO_2 and (B) Fe K-edge Fourier-filtered EXAFS and the Fourier transform of well-defined Fe_2O_3/TiO_2.

seem to demonstrate that the presence of rutile in the TiO_2 is significant, probably much more than that determined by XRD (15%) since formation of short-range-ordered rutile and/or anatase units is fundamentally not observable by such a technique as XRD. In comparison with the crystals, the three Ti–Ti shells approximately corresponding and the Ti–Ti distances in rutile and anatase, respectively [10], will give a fair knowledge of the structural model of the TiO_2, in particular its exposed surface for iron deposition. Further studies concerning the geometric description are underway.

It is clear from table 2 that the irons on the Fe_2O_3/TiO_2 are in six coordination. The average Fe–O bond length is 2.02 Å. 1.7 nearest Ti neighbors at 2.69 Å and 0.9 titanium at 3.58 Å demonstrate that the irons are deposited on the TiO_2 surface and 1.4 nearest Fe neighbors at 2.95 Å and 2.2 irons at 4.45 Å indicate that the irons are well separated from each other. The fact that both Ti and Fe neighbors are simultaneously observed within 3 Å accompanied by a relatively small CN (<2) highly suggests a two-dimensional arrangement for the iron ensembles on the surface. In case an energetically most favorable surface of the TiO_2 is determined, a geometrical model for the Fe_2O_3/TiO_2 will be available following the way shown in

Table 2
EXAFS-derived parameters (CN: coordination number; *R*: shell radius; DW: Debye–Waller factor) for the TiO_2 used as support, well-defined Fe_2O_3/TiO_2 and the Fe/TiO_2 pre-reduced at 723 and 773 K

Sample	Shell	CN	*R* (Å)	DW	*R*-factor
TiO_2	Ti–O	2.9(3)	1.906(7)	0.0	0.06
	Ti–O	4.4(5)	2.020(7)	0.002	
	Ti–O	3.6(11)	2.71(3)	0.005	
	Ti–Ti	3.2(9)	3.31(2)	0.007	
	Ti–Ti	1.7(7)	3.68(3)	0.004	
	Ti–Ti	2.9(15)	4.84(6)	0.008	
Fe_2O_3/TiO_2	Fe–O	3.7(6)	1.95(1)	0.004	0.10
	Fe–O	2.3(6)	2.13(2)	0.002	
	Fe–Ti	1.7(9)	2.69(4)	0.012	
	Fe–Fe	1.4(12)	2.95(6)	0.013	
	Fe–Ti	0.9(10)	3.58(8)	0.006	
	Fe–Fe	2.2(13)	4.45(4)	0.005	
Fe/TiO_2 reduced at 723 K	Fe–O	1.8(6)	1.90(1)	0.002	0.08
	Fe–O	1.8(4)	2.04(2)	0.001	
	Fe–Fe	2.2(5)	2.48(1)	0.005	
	Fe–Fe	6.0(15)	2.78(2)	0.013	
Fe/TiO_2 reduced at 773 K	Fe–O	1.8(6)	1.94(2)	0.003	0.09
	Fe–O	1.8(6)	2.07(2)	0.001	
	Fe–Fe	2.0(5)	2.48(1)	0.006	
	Fe–Fe	6.1(15)	2.77(2)	0.015	

fig. 1. However, since properties of surface groups and sites can be interpreted by considering the central cation and its nearest oxygen environment only [11], the present data is thought to be enough to predict that the surface geometry of well-defined iron oxides described by fig. 1 is undoubtedly effective for Fe_2O_3/TiO_2. It indicates that formation of geometrically stable FeO_6 units is favored by the TiO_2 surface and is the main reason for poor catalytic activities for well-defined iron catalysts.

Fe K-edge EXAFS-derived Fourier transforms shown in fig. 7 indicate that the catalysts pretreated at 723 and 773 K have much the same spectral features, but that pretreated at 823 K is really different. In comparison with the transform of the well-defined one shown in fig. 6, it is easy to see that the nearest oxygen contributions surrounding the Fe site on the Fe/TiO_2 are greatly reduced. The most intense peak is not contributed by the nearest oxygens but the nearest iron neighbors and the Fe–O shells only give a weak peak at about 1.5 Å (not corrected for the phase shift). The best fits (fig. 8) to the Fourier transform and the Fourier-filtered EXAFS of the Fe/TiO_2 (5 wt%) pretreated at an appropriate temperature of 773 K reveals totally 3.6 nearest oxygen neighbors at 2.01 ± 0.02 Å, 2 nearest

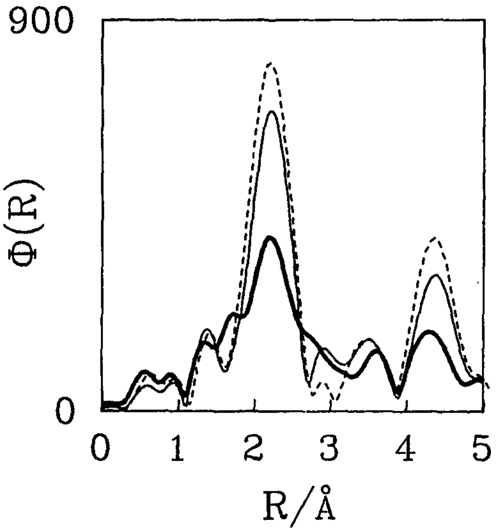

Fig. 7. The Fourier transforms of the Fe/TiO_2 pre-reduced at 723 K (dashed line), 773 K (solid line) and 823 K (bold line).

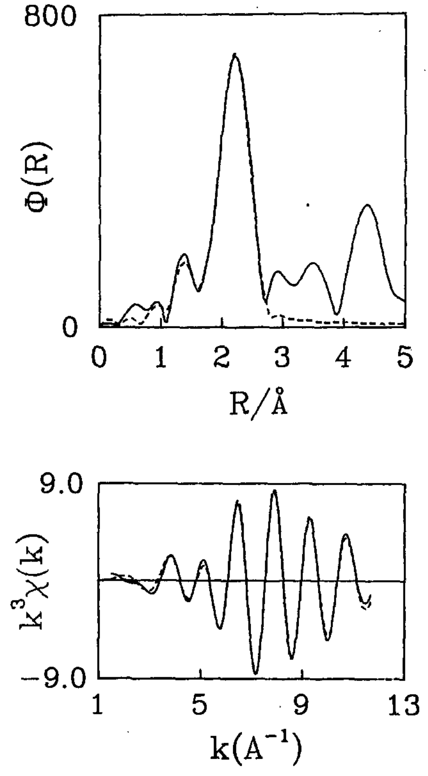

Fig. 8. The best fits to Fe K-edge Fourier-filtered EXAFS and the Fourier transform of the Fe/TiO_2 pre-reduced at an appropriate temperature of 773 K.

irons at 2.48 ± 0.01 Å, and 6 next nearest irons at 2.77 ± 0.02 Å, see table 2. This means that at least about 25% irons on the Fe/TiO_2 are zerovalent and that the others are cations. Otherwise, on well-defined Fe_2O_3/TiO_2, no Fe–Fe shell at 2.48 Å corresponding to zerovalent irons was found. The shortest distance between iron cations on Fe_2O_3/TiO_2 is 2.95 Å, but is found to be only 2.77 Å on the Fe/TiO_2. The present EXAFS-derived data is therefore in good agreement with the Mössbauer results and suggests the formation of Fe(0) and/or α-Fe. In comparison with the well-defined one, the significantly reduced coordination number of the first Fe–O shell is expected as specified at the beginning of this paper, but it is still difficult to understand why the average Fe–O bond length remains the same. The lower coordination number 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/TiO_2. Since the Fe^{2+}-A in $FeTiO_3$ determined by the Mössbauer spectra is known to be in six coordination, the lower coordination number of the nearest oxygens is therefore thought to be due mainly to the unsaturated coordination of Fe^{2+}-B, probably by the aid of zerovalent iron atoms.

Interestingly, it has been found from the best fits (table 2) that the Fe–O bond length on the catalyst reduced at 723 K is only 1.97 Å. Therefore, an increase in the Fe–O bond strength for this catalyst makes the catalytic activity lower.

In conclusion, the Fe/TiO_2 as described exhibits a good catalytic activity in 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 temperatures of the precursors. The active phase is coordinatively unsaturated cations, but α-Fe may be also closely related. As suggested by the reaction studies, it is the CO that reacts with H_2 to give hydrocarbons. Since zerovalent irons, for example the irons on cluster-derived Fe/Al_2O_3 [6], have shown good selectivity for lower olefins in CO hydrogenation, the combination of α-Fe and Fe^{2+}-B may significantly inhibit the secondary hydrogenation, and therefore lead the catalyst to convert the high ratio H_2/CO to hydrocarbon products rather than simply to CH_4. On the other hand, alternative rearrangement of the two phases in a proper way may significantly relax the Fe–O bonds, resulting in higher catalytic activity for the catalyst. However, the formation of predominantly $FeTiO_3$ phase may damage the proper structure at the interface and thus finally make the catalyst inactive.

Acknowledgement

The project was supported by the National Natural Science Foundation, China. We are grateful to the Photon Factory for the use of BL-7C facilities. We thank Dr. T. Tanaka and Professor M. Nomura for experimental assistance.

References

[1] W.-J. Ji, Y. Kou, S. Shen, S. Li and H.-L. Wang, Stud. Surf. Sci. Catal. 75 (1993) 2059.
[2] Y. Kou, H.-L. Wang, J.-Z. Niu and W.-J. Ji, J. Phys. Chem., submitted.
[3] Y. Kou, Z.-H. Sou, J.-Z. Niu, W.-Z. Zhang and H.-L. Wang, Catal. Lett. 35 (1995) 271.
[4] B.C. Lippens and J.H. de Boer, Acta Cryst. 17 (1964) 1312.
[5] H. Knözinger and P. Ratnasamy, Catal. Rev. Sci. Eng. 17 (1978) 31.
[6] Y. Kou, H.-L. Wang, M. Te, T. Tanaka and M. Nomura, J. Catal. 141 (1993) 660.
[7] Y. Kou, Z.-H. Suo and H.-L. Wang, J. Catal. 149 (1994) 247.
[8] D.G. Rethwisch and J.A. Dumesic, J. Phys. Chem. 90 (1986) 1863.
[9] S.A. Stevenson, S.A. Goddard, M. Arai and J.A. Dumesic, J. Phys. Chem. 93 (1989) 2058.
[10] C.L. Christ, *Descriptive Crystal Chemistry* (Wiley, New York, 1989).
[11] H. Knözinger, in: *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*, eds. J.-M. Basset and B.C. Gates (Kluwer Academic, Dordrecht, 1988) p. 44.