Structure–Activity Relationship of Iron Titanate Catalysts in the Selective Catalytic Reduction of NO_x with NH_3^{\dagger}

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A series of iron titanate catalysts, $Fe_aTi_bO_x$, with different Fe-Ti molar ratios are synthesized via a facile coprecipitation method and tested for the selective catalytic reduction (SCR) of NO_x with NH₃. The structural properties and redox behavior of the serial catalysts are comprehensively characterized. Comparing with pristine TiO₂ and Fe₂O₃, the coexistence of iron and titanium species is favorable to form crystallites with specific Fe-O-Ti structure, which is highly active for the NH₃-SCR reaction. Fe₄Ti₄O_x catalyst with a Fe-Ti molar ratio of 1:1 shows the highest intrinsic activity, due to its smallest particle size, enhanced oxidative ability of Fe³⁺, highest mobility of lattice oxygen, and abundant acid sites. The correlation between catalytic performance and reactant adsorption capability/conformation is also studied, indicating that an appropriate method to improve the low temperature SCR activity of iron titanate catalyst is to enhance the adsorption ability of NO_x as monodentate nitrate on catalyst surface.

Introduction

Preparation and application of mixed metal oxides have attracted much attention from many researchers with regard to their special magnetic, electrical, optical, and catalytic characteristics, which may be markedly different from those of pristine bulk oxides. Nowadays, more and more studies are focusing on the synthesis of iron-titanium oxide composites by using different preparation methods, including wet impregnation,¹ hydrothermal method,¹ coprecipitation,² sol-gel process,³ chemical vapor deposition,⁴ ultrasound irradiation,⁵ and hydrolysisfreezing techniques.⁶ Among these methods, the coprecipitation process is very easy to operate, which can produce homogeneously dispersed compositions in the bulk phase and on the surface. The resultant iron-titanium oxide composites are expected to be utilized in the fields of magnetic semiconductors,⁷ magneto-optical semiconductors,8 and catalysis, such as photocatalytic degradation of organic pollutants,9,10 photoelectrochemical generation of hydrogen from water, 11,12 catalytic isomerization,³ and catalytic oxidation.^{13,14} The Fe₂O₃-TiO₂ catalysts prepared from different precursors and synthesis methods were also used in the selective catalytic reduction (SCR) of NO_x with NH₃ to eliminate NO_x from flue gas for environmental protection.15,16

In our previous study, we have successfully synthesized a novel iron titanate catalyst using ferric nitrate and titanium sulfate as precursors through coprecipitation method, which was highly active and selective for the SCR of NO_x with NH₃ in the medium temperature range.¹⁷ The durability of H₂O/SO₂ at 300 °C was also tested for 48 h, during which no decline of NO_x conversion was observed.¹⁷ This cheap and environmentalfriendly catalyst is promising to be used in the catalytic removal of NO_x from stationary and mobile sources after molding, contributing to the reduction of acid rain and photochemical smog.¹⁸ The influence of different titanium precursors (Ti(SO₄)₂ vs TiCl₄) and preparation methods (coprecipitation vs wet impregnation) on the structure and activity has been also clearly clarified.¹⁹ However, the molar ratios of iron and titanium species in these catalysts were fixed at 1:1, because our previous expectation was to synthesize homogeneously dispersed Fe–O-Ti structures with specific catalytic performance. This is not advantageous to carry out further study about the structure– activity relationship of iron titanate catalysts in the SCR reaction without optimizing the Fe–Ti molar ratios.

In this study, serial iron titanate catalysts $Fe_aTi_bO_x$ with different Fe-Ti molar ratios (a:b = 0:4, 1:4, 2:4, 4:4, 4:2, 4:1, 4:0) are synthesized and tested for the SCR of NO_x with NH_3 . The structural properties are first characterized by N₂ physisorption, powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and selected area electron diffraction (SAED) methods. Then the redox properties are characterized by X-ray photoelectron spectroscopy (XPS) and H₂ temperature programmed reduction (H₂-TPR). Finally, the correlation between catalytic performance and reactant adsorption capability/conformation on different catalysts is fully studied using in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) of NH₃ and NO_x adsorption together with the temperature programmed desorption of NH₃ and NO_x (NH₃/NO_x-TPD). The better understanding of the structure-activity relationship over iron titanate catalysts will be beneficial to the further improvement of low temperature SCR activity in catalyst redesign and practical use.

Experimental Section

Catalysts Preparation and Activity Test. $Fe_aTi_bO_x$ serial catalysts with different Fe-Ti molar ratios were facilely synthesized by conventional coprecipitation method using $Fe(NO_3)_3 \cdot 9H_2O$ ($\geq 98.5\%$) and $Ti(SO_4)_2$ ($\geq 96\%$) as precursors and $NH_3 \cdot H_2O$ (25 wt %) as precipitator. After the pH of the mixed solution rose to 10 in the coprecipitation process, the precipitate cakes were first filtrated and washed by distilled water, and then desiccated at 100 °C for 12 h and calcined at

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400 °C for 6 h under air conditions (the heating rate kept at 5 °C/min). The calcined samples were crushed and sieved to 20-40 mesh for activity tests in the NH₃-SCR reaction in a fixed-bed quartz tube reactor. The reaction conditions were controlled as follows: 0.6 mL of catalysts, 500 ppm NO, 500 ppm NH₃, 5 vol % O₂, N₂ as the balance, and a gas hourly space velocity (GHSV) of 50000 h⁻¹. The effluent gas including NH₃, NO, NO₂, and N₂O was continuously analyzed using an FTIR spectrometer (Nicolet Nexus 670) equipped with a heated, low volume multiple-path gas cell (2 m). During the SCR reaction process, no other nitrogen-containing component besides of NH₃, NO, NO₂, and N₂O was detected in the effluent gas. All experimental data were recorded when the steady-state SCR reaction rate was achieved. NO_x conversion (X_{NOx}) and N₂ selectivity (S_{N_2}) were calculated as follows: $X_{NOx} = (1 - 1)^{-1}$ $[NO_x]_{out}/[NO_x]_{in}) \times 100\%$ with $[NO_x] = [NO] + [NO_2]; S_{N_2} =$ $([NO]_{in} + [NH_3]_{in} - [NO_2]_{out} - 2[N_2O]_{out})/([NO]_{in} + [NH_3]_{in})$ \times 100%.

Structural Characterizations. N₂ adsorption–desorption isotherms were obtained at -196 °C using a Quantachrome Autosorb-1C instrument. Prior to N₂ physisorption, the catalysts were degassed at 300 °C for 5 h. Surface areas were determined by BET equation in 0.05–0.35 partial pressure range. Pore volumes, average pore diameters, and pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms. Powder XRD patterns were measured on a Rigaku D/max-RB diffractometer (Japan, Cu K_a as radiation resource). The data of 2 θ from 10 to 90° were collected at 4°/min with the step size of 0.02°. The TEM images with low magnification were obtained on a H-7500 TEM (Hitachi) and JEOL 2011 TEM (JEOL). The HR-TEM images with high magnification and SAED patterns were obtained on JEOL 2011 TEM (JEOL).

Redox Behavior Characterizations. XPS were recorded on a scanning X-ray microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al K_a radiation. Binding energies of Fe 2p, Ti 2p, and O 1s were calibrated using the C 1s peak (BE = 284.8 eV) as standard. H₂-TPR experiments were conducted over 100 mg of catalysts, and the H₂ signal (m/z = 2) was monitored online using a quadrupole mass spectrometer (HPR20, Hiden Analytical Ltd.). Prior to the TPR procedure, the catalysts were pretreated in a flow of 20 vol % O₂/He (30 mL/min) at 300 °C for 0.5 h and cooled down to room temperature. Then the temperature was raised linearly to 950 °C at the rate of 10 °C/ min in a flow of 5 vol % H₂/Ar (30 mL/min).

Reactant Adsorption Capability/Conformation. In situ DRIFTS of NH₃ and NO + O₂ adsorption over Fe_aTi_bO_x serial catalysts were performed on an FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 400 °C in a flow of 20 vol % O₂/N₂ for 0.5 h and then cooled down to 150 °C. The background spectrum was collected in flowing N2 atmosphere and subtracted from the sample spectrum. Then the samples were exposed to a flow of 500 ppm NH₃/N₂ or 500 ppm NO + 5 vol % O_2/N_2 (300 mL/ min) for 1 h and then purged by N2 for another 0.5 h. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. NH₃-TPD and NO_x-TPD were also performed using the quadrupole mass spectrometer (HPR20, Hiden Analytical Ltd.) to record the signals of NH_3 (m/z = 16 for NH_2) and NO_x (m/z = 30 for NO and NO₂). Prior to the TPD procedure, the samples (100 mg) were pretreated in a flow of 20 vol % O₂/He



Figure 1. NO_x conversion as a function of temperature in the NH₃-SCR reaction on Fe_aTi_bO_x serial catalysts. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol %, N₂ balance, total flow rate 500 mL/min, and GHSV = 50000 h⁻¹.

(30 mL/min) at 300 °C for 0.5 h and cooled down to room temperature. Then the samples were exposed to a flow of 2500 ppm NH₃/Ar or 2500 ppm NO + 10 vol % O₂/Ar (30 mL/min) for 1 h and then purged by Ar for another 1 h. Finally, the temperature was raised linearly to 500 °C in Ar flow at a rate of 10 °C/min.

Results and Discussion

Catalytic Performance. The $Fe_aTi_bO_x$ serial catalysts with different Fe-Ti molar ratios were tested in the NH3-SCR of NO_x and the results are shown in Figure 1. Pristine TiO₂ showed nearly no activity below 350 °C and only 30% NO_x conversion at as high as 400 °C. With a relatively small amount of Fe contained in Fe₁Ti₄O_x, the SCR activity was greatly enhanced, implying the formation of new active phase due to the interaction between iron and titanium species. Increasing the amount of Fe from $Fe_1Ti_4O_x$ to $Fe_4Ti_1O_x$ resulted in monotonous enhancement of low temperature activity below 300 °C and simultaneous decrease of high temperature activity above 300 °C. At the same time, the selectivity from NOx to N2 also showed some decrease when the Fe amount was larger because of the formation of N₂O and NO₂ probably due to the occurrence of unselective oxidation of NH₃ (see Figure S1 in Supporting Information). Therefore, there should be a compromise between the SCR activity and N2 selectivity when considering the Fe-Ti molar ratios. Accordingly, both of $Fe_4Ti_4O_x$ and $Fe_4Ti_2O_x$ appear to be suitable for practical applications. As for pristine Fe_2O_3 , the operation temperature window was rather narrow and the maximum NO_x conversion was only 60%, with the lowest N_2 selectivity among all samples (Figure S1). These results suggest that the coexistence of iron and titanium species is indeed very important for the SCR reaction due to the formation of iron titanate phases, which were validated as Fe₂TiO₅ or FeTiO₃ crystallites with specific Fe-O-Ti structure in our previous studies.^{17,19} The experimental results in the following characterization sections will supply us more information about the structure-activity relationship of these iron titanate catalysts in the SCR reaction.

In iron titanate catalysts, the Fe^{3+} species were the active centers with strong redox ability and the Ti⁴⁺ species mainly played the role as acid sites to adsorb reducing agent NH₃.¹⁹ To further elucidate the intrinsic catalytic activity of these iron titanate catalysts in the SCR reaction, the turnover frequency

TABLE 1: Structural Parameters of $Fe_aTi_bO_x$ Serial Catalysts and Specific Catalytic Activity (TOF) in the NH₃-SCR of NO_x at 150 °C

samples	$\frac{S_{\rm BET}}{({\rm m}^2 \cdot {\rm g}^{-1})^a}$	pore volume $(cm^3 \cdot g^{-1})^b$	pore diameter (nm) ^c	TOF $(10^{-3} \cdot s^{-1})^a$ at 150 °C
TiO ₂	103.5	0.20	7.6	
$Fe_1Ti_4O_x$	227.9	0.30	5.1	0.45
$Fe_2Ti_4O_x$	275.2	0.37	5.2	0.42
$Fe_4Ti_4O_x$	236.6	0.47	7.9	0.70
$Fe_4Ti_2O_x$	269.6	0.45	6.6	0.38
$Fe_4Ti_1O_x$	200.3	0.34	6.6	0.38
Fe_2O_3	42.5	0.21	19.4	

^{*a*} BET surface area. ^{*b*} BJH desorption pore volume. ^{*c*} Average pore diameter. ^{*d*} The number of active iron sites over catalyst surface in the TOF calculation was obtained from XPS (surface atomic concentration, Table 2) and BET surface area data. According to our previous study,¹⁷ the BET surface area data. According to our previous study,¹⁷ the BET surface area over Fe₄Ti₄O_x-500 °C was nearly 60% of that over Fe₄Ti₄O_x-400 °C, yet similar apparent SCR activity was obtained over these two samples. Therefore, in this study it was assumed that ca. 60% of surface areas over Fe_aTi_bO_x serial catalysts was effective in the real SCR reaction. On the basis of the surface atomic concentration data, the total surface area of Fe³⁺ sites can be calculated. According to this result, the number of Fe³⁺ sites can be further obtained by dividing the surface area of each Fe³⁺ cation.

TABLE 2: Semiquantitative Analysis of Surface AtomicConcentration (% in molar ratio) over $Fe_a Ti_b O_x$ SerialCatalysts Derived from XPS Data

samples	Fe (%)	Ti (%)	0 (%)	S (%)
TiO ₂		28.0	71.9	0.12
$Fe_1Ti_4O_x$	3.7	22.8	73.6	0.00
$Fe_2Ti_4O_x$	6.2	20.1	73.7	0.03
$Fe_4Ti_4O_x$	8.4	15.4	76.2	0.00
$Fe_4Ti_2O_x$	13.0	11.1	75.9	0.05
$Fe_4Ti_1O_x$	15.3	7.0	77.7	0.00
Fe_2O_3	21.5		78.5	

(TOF) of NO_x over each active Fe^{3+} site was calculated and the results are shown in Table 1. Although the number of Fe³⁺ sites derived from this method was relatively rough, and the heat/mass transfer phenomena were probably involved in the activity test procedure making the TOF data imprecise, these data are still comparable internally if the reaction conditions were controlled exactly the same, providing some useful information about the intrinsic catalytic activity of these serial $Fe_aTi_bO_x$ catalysts. At 150 °C, the $Fe_4Ti_4O_x$ catalyst possessed the highest TOF, indicating that the Fe-O-Ti structure with Fe-Ti molar ratio being 1:1 is indeed highly active for the NO_x reduction process, especially in the low temperature range (<200 °C). For Fe₄Ti₂O_x and Fe₄Ti₁O_x samples with Fe–Ti molar ratio exceeding 1:1, some aggregated Fe₂O₃ particles might form during the preparation process, thus leading to the decrease of TOF values. An appropriate molar ratio of iron and titanium species is an important factor to be considered in the catalyst design process, which is crucial to the enhancement of intrinsic catalytic activity of $Fe_aTi_bO_x$ catalysts.

Structural Characterizations

N₂ Physisorption. Figure 2A shows the N₂ adsorption– desorption isotherms of $Fe_a Ti_b O_x$ serial catalysts measured at liquid nitrogen temperature. For pristine TiO₂, the isotherms resembled closely with type IV isotherms according to the IUPAC classification,²⁰ which are typical for mesoporous materials (2–50 nm). The hysteresis loop exhibited typical H2



Figure 2. (A) N₂ adsorption–desorption isotherms and (B) pore size distributions of $Fe_a Ti_b O_x$ serial catalysts.

type, indicating the presence of an ink-bottle-shaped pore structure.²⁰ With the increase of Fe amount from $Fe_1Ti_4O_x$ to $Fe_4Ti_1O_x$, the isotherms in the high P/P_0 range shifted from a type IV to type II pattern. This indicates the formation of some macropores (>50 nm) besides of mesopores, which was probably due to the aggregation of small oxide particles in these samples. The hysteresis loops also shifted from H2 type to H3 type, suggesting the presence of slit-shaped pore structure in iron titanate catalysts. Besides, the closure point of the hysteresis loops of these samples occurred at lower P/P_0 compared with that of TiO_2 , indicating the more abundant of micropores (<2 nm) due to the interaction of iron and titanium species. The broad pore size distribution and the possession of appropriate ratios of micropores, mesopores, and macropores is an important reason for the high SCR activity over these iron titanate catalysts. Much more inner surface area and pore volume can be supplied by micropores plus mesopores in the SCR reaction, and the mass transfer is much easier with the existence of some macropores. Therefore, the optimal pore size distribution of these iron titanate catalysts should be a majority of micropores and mesopores together with a minority of macropores, e.g., similar to the pore size distribution of $Fe_4Ti_4O_x$. As for pristine Fe_2O_3 , the isotherms returned to type IV together with the presence of H2 type hysteresis loop, similar to those of TiO2. The closer point of this hysteresis loop at much higher P/P_0 implies that the average pore size of Fe_2O_3 is much larger than that of TiO_2 .

Calculated from the isotherms, the BET surface areas, pore volumes, and average pore diameters of all samples are shown in Table 1. The iron titanate catalysts indeed have larger surface areas (>200 m²/g), more abundant pore volumes, and appropriate pore diameters compared with those of pristine TiO₂ and Fe₂O₃. The pore size distributions shown in Figure 2B imply that the active crystallite phases formed in iron titanate catalysts mainly possess micropores and mesopores with peak values near 3.4 nm. The excess iron species in Fe₄Ti₂O_x and Fe₄Ti₁O_x might be in the form of aggregated Fe₂O₃ particles, thus resulting in the bimodal mesopore size distributions with the peak values at 3.4 and 4.9 nm.

PXRD. The PXRD patterns of $Fe_a Ti_b O_x$ serial catalysts are shown in Figure 3. Pristine TiO₂ and Fe_2O_3 displayed well-defined diffraction peaks attributed to typical anatase and hematite, respectively, which is in accordance with the low surface areas and pore volumes in Table 1. The coexistence of iron and titanium species resulted in the formation of amorphous or crystallite phases exhibiting large broad bump diffraction



Figure 3. PXRD results of $Fe_a Ti_b O_x$ serial catalysts.

patterns, which are helpful to enhance the surface areas, the pore volumes, and thus the SCR activity. Even a small amount of iron species in titanium oxide or titanium species in iron oxide, such as $Fe_1Ti_4O_x$ and $Fe_4Ti_1O_x$, could lead to the formation of homogeneously dispersed crystallites because of the similar ion radii of Fe^{3+} (0.645 Å) and Ti^{4+} (0.605 Å).^{11} When the Fe-Ti molar ratio increased from 1:4 to 4:4, the position of the main broad bump shifted toward higher diffraction degree, as shown in the enlarged inserted figure. According to the JCPDS standard cards, the active phases in $Fe_4Ti_4O_x$ are mainly composed of Fe₂TiO₅ or FeTiO₃ crystallites,^{17,19} because these species mainly show diffraction peaks at the marked positions (**▼●**). The continuous increasing of Fe−Ti molar ratio from 4:2 to 4:1 shifted the broad bump toward higher diffraction degree further, which is much closer to the main positions of hematite. This result confirms that small aggregated Fe₂O₃ particles indeed exist in the samples with excess iron species, resulting in the much lower TOF in NO_x reduction process. The UV-vis diffuse reflectance absorption spectroscopy (UV-vis DRS) in Figure S2 (Supporting Information) also support this conclusion.

TEM, HR-TEM, and SAED. The morphologies of $Fe_aTi_bO_x$ serial catalysts were characterized by TEM and HR-TEM. The TEM images are shown in Figure 4, together with the inserted SAED patterns. Pristine TiO2 in Figure 4a mainly presented in the form of uniform particles with diameters around 15 nm. The HR-TEM image showed that the TiO₂ particle was in a two-dimensional hexagonal shape with legible lattice fringes. Through measurement, the interplanar distance is confirmed to be 0.355 nm, which corresponds well to the (101) plane of anatase TiO2.21,22 The discrete electron diffraction spots in SAED pattern indicate that these TiO₂ particles are highly crystallized mainly in polycrystal structures, which is in accordance with the XRD result in Figure 3. From panels b to f in Figure 4, the coexistence of iron and titanium species resulted in much smaller roundlike oxide particles below 10 nm, which easily got aggregated as floccules. The HR-TEM images were also difficult to discern; therefore we lined out the profiles of the particles by hand for the sake of clear identification. No legible but some intercrossed lattice fringes were observed for all iron titanate catalysts, and the shapes of the electron diffraction rings indicate that all samples are in noncrystal or crystallite structures. This will provide more surface areas and active sites for the occurrence of SCR reaction over them. Due to the noncrystal or crystallite states and the small particle sizes of these samples, no detailed structural information could be obtained easily from the HR-TEM images. As for pristine Fe₂O₃, the particles were mainly present in two-dimensional elliptical shapes with a broad



Figure 4. TEM, HR-TEM, and SAED results of $Fe_aTi_bO_x$ serial catalysts: (a) TiO₂, (b) $Fe_1Ti_4O_x$, (c) $Fe_2Ti_4O_x$, (d) $Fe_4Ti_4O_x$, (e) $Fe_4Ti_2O_x$, (f) $Fe_4Ti_1O_x$, (g) Fe_2O_3 , (h) average particle sizes obtained from TEM images.

size distribution. The interplanar distance measured from the HR-TEM image is 0.37 nm, corresponding well to the (012) plane of hematite Fe_2O_3 .^{21,23,24} The clear thin electron diffraction rings along with discrete electron diffraction spots indicate that these Fe_2O_3 particles are also in polycrystal structures. The average particle sizes of all samples obtained from TEM images are presented in Figure 4h. $Fe_4Ti_4O_x$ possesses the smallest average particle size due to the strongest interaction between iron and titanium species when the Fe–Ti molar ratio is 1:1.

Redox Behavior Characterizations

XPS. The surface atomic concentrations and valence states of Fe, Ti, and O elements in $Fe_aTi_bO_x$ serial catalysts were characterized by XPS, and the results are shown in Table 2 and Figure 5. For iron-containing samples in Figure 5A, two well-



Figure 5. XPS results of (A) Fe 2p, (B) Ti 2p, and (C) O 1s of $Fe_aTi_bO_x$ serial catalysts (accuracy of binding energies: ± 0.2 eV).

defined peaks ascribed to Fe 2p_{3/2} (710.8-711.4 eV) and Fe 2p_{1/2} (724.4-725.0 eV) showed up. The binding energies of these two peaks correspond well with characteristic Fe³⁺ according to literature.^{25,26} Over $Fe_1Ti_4O_x$, both of the Fe $2p_{3/2}$ and Fe 2p_{1/2} peaks possessed the highest binding energies, which means that the electron cloud of iron species in this sample has the severest deviation due to the inductive effect of titanium species. Therefore, the average oxidative ability of iron species in Fe₁Ti₄O_x should be the strongest among all samples, which is beneficial to the oxidation of NO to NO₂. The resulting NO₂ could take part in the "fast SCR" according to the overall reaction as NO + NO₂ + 2NH₃ \rightarrow 2N₂ + 3H₂O,^{27,28} leading to the increase of low temperature SCR activity. Among $Fe_a Ti_b O_x$ serial catalysts, although Fe₁Ti₄O_x showed the highest binding energy of Fe³⁺ species, the reactant adsorption ability of this catalyst was not optimal. Therefore, it is reasonable to obtain the lower TOF and apparent NO_x conversion over this sample. With the increase of Fe amount from $Fe_1Ti_4O_x$ to $Fe_4Ti_1O_x$, the surface Fe concentration showed an obvious increase from 3.7 to 15.3% in molar ratio, indicating the occurrence of surface Fe enrichment. At the same time, the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ showed slight shift toward the low energy direction, because the inductive effect of the titanium species is getting weaker when the Ti amount is smaller. Although the average oxidative ability of iron species is slightly decreased in this process, the number of active sites in the SCR reaction is increased. Therefore, this XPS result is not in contradiction to the monotonously increased apparent low temperature activity. As for pristine Fe_2O_3 , the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were the lowest at 710.8 and 724.4 eV, respectively, indicating again that the coexistence of iron and titanium species is very important to enhance the oxidative ability of iron titanate catalysts.

For titanium-containing samples in Figure 5B, two welldefined peaks ascribed to Ti $2p_{3/2}$ (458.4–458.9 eV) and Ti $2p_{1/2}$ (464.2–464.8 eV) of characteristic Ti⁴⁺ showed up,^{26,29} and the variation trend of Ti 2p binding energies with the increasing of Fe–Ti molar ratios was nearly the same as those of Fe 2p in Figure 5A. Without iron species, the pristine TiO₂ possessed the highest Ti 2p binding energies at 458.9 and 464.8 eV. When the titanium species coexisted with iron species from Fe₁Ti₄O_x to Fe₄Ti₁O_x, the binding energies of Ti 2p showed obvious shift toward the low energy direction, owing to the inductive effect of titanium species to "pull" the electron cloud of iron species closer. Compared with the pristine Fe₂O₃ and TiO₂, the



Figure 6. H₂-TPR results of $Fe_aTi_bO_x$ serial catalysts: (A) full observation, (B) deconvoluted results of low temperature reduction peaks.

heightening of Fe 2p binding energies and simultaneous lowering of Ti 2p binding energies were also observed over Fe_xTiO_y prepared from TiCl₄ precursor and Fe_2O_3/TiO_2 prepared by impregnation method in our previous study.¹⁹ Similar phenomenon was also observed in several iron-titanium oxide composites prepared by other researchers,^{2.5,30} some of whom concluded that the lowering of Ti 2p binding energies might be owing to the formation of Fe-O-Ti bond.⁵ By far, we consider that this phenomenon universally occurs over iron-titanium containing catalysts and the specific Fe-O-Ti structure is highly active in the SCR reaction, although this was not realized in previous studies.

As shown in Figure 5C, the XPS of O 1s in $Fe_aTi_bO_x$ serial catalysts were also recorded and deconvoluted into two groups of sub-bands by searching for the optimum combination of Gaussian bands with the correlation coefficients (r^2) above 0.99 (PeakFit, Version 4.12, SeaSolve Software Inc.). The sub-bands at lower binding energies (529.8-530.2 eV) corresponded to the lattice oxygen O^{2-} (denoted as O_{β}), and the ones at higher binding energies (531.1-531.6 eV) corresponded to the surface adsorbed oxygen (denoted as O_{α}).³¹ As we described above, the inductive effect of electron cloud around oxygen species by titanium species also existed in titanium containing samples, because the binding energies of O 1s bands in TiO₂ to Fe₄Ti₁O_x were higher than those in Fe₂O₃ as shown in Figure 5C. Usually, the surface oxygen $O_{\boldsymbol{\alpha}}$ is more reactive in oxidation reactions due to its higher mobility than lattice oxygen O_{β} ,^{32,33} which is also beneficial to the NO oxidation to NO_2 in the SCR reaction. In this process, NO could react with reactive surface oxygen on the Fe³⁺ sites with enhanced oxidative ability due the inductive effect of Ti4+ to produce adsorbed NO2 or nitrate species, further participating in the following reactions with NH₃. Therefore, the relative concentration ratios of $O_{\alpha}/(O_{\alpha} + O_{\beta})$ over all samples are calculated and listed in the left side of Figure 5C. For iron- and titanium-containing samples (except Fe₁Ti₄O_x with relatively low Fe content), the O_{α}/(O_{α} + O_{β}) ratios were much higher than that of pristine TiO₂, indicating the presence of more abundant surface oxygen. This might be beneficial to the enhancement of NO oxidation and thus the SCR activity, especially in the low temperature range below 200 °C.

H₂-TPR. The reducibility of $Fe_a Ti_b O_x$ serial catalysts was investigated by the H₂-TPR method, and the results are shown in Figure 6. As shown in Figure 6A, pristine TiO₂ showed no

obvious H₂ consumption peak in the whole temperature range that we investigated; therefore, all H₂ consumption peaks that occurred over other samples could be attributed to the reduction of iron species. With the increasing of Fe amount from $Fe_1Ti_4O_x$ to $Fe_4Ti_4O_x$, obvious overlapped reduction peaks in the range of 300-500 °C showed up, and the temperatures of the peak values gradually decreased as the arrows show. The continuous increasing of Fe amount from $Fe_4Ti_4O_x$ to $Fe_4Ti_1O_x$ further decreased the temperatures of the peak values, but broad reduction peaks in the high temperature range gradually occurred. As for pristine Fe₂O₃, the temperature of the peak value returned to the relatively high side, and a large broad reduction peak around 725 °C showed up. In order to confirm the detailed reduction processes of iron species, we calculated the H_2/Fe ratios (mol/mol) in the temperature range that the dashed rectangle shows. From $Fe_1Ti_4O_x$ to $Fe_4Ti_4O_x$, the H₂/Fe ratios are above 0.5 but below 1.5, indicating that the Fe³⁺ species have been totally converted into Fe2+ until 500 °C, and then partial Fe²⁺ species have been converted into metallic Fe⁰. Further reduction did not happen at higher temperatures that we investigated, probably due to the formation of compact ilmenite or metallic Fe⁰ on the catalyst surface blocking the H₂ diffusion into the bulk phase. For $Fe_4Ti_2O_r$ and $Fe_4Ti_1O_r$, the H₂/Fe ratios are above 0.17 but below 0.5, suggesting that the Fe^{3+} species in these two samples have been converted into iron species with intermediate valence similar to that in Fe₃O₄ (denoted as $Fe^{(3-\delta)+}$ afterward, in which $\delta = 1/3$), and then partial $Fe^{(3-\delta)+}$ species have been converted into Fe^{2+} . The broad reduction peaks at higher temperatures are possibly due to the further reduction of $Fe^{(3-\delta)+}$ to Fe^{2+} . This result shows that although the temperatures of the peak values in the range of 300-500 °C decreased with the increasing Fe amount, the reducibility of the catalysts was actually lowered when the Fe-Ti molar ratio was above 1:1. Accordingly, the mobility of oxygen species in $Fe_4Ti_4O_x$ is the highest due to the strongest interaction between iron and titanium species, producing severest structural distortion and most abundant oxygen defects. As for pristine Fe_2O_3 , the H₂/Fe ratio in the rectangle area is 0.17, perfectly corresponding to the reduction process from Fe₂O₃ to Fe₃O₄. The large broad reduction peak centered at 725 °C is due to the further reduction to FeO and partial Fe⁰. This result suggests again that the coexistence of iron and titanium species can significantly enhance the oxidative ability of Fe³⁺ species owing to the formation of Fe-O-Ti structure.

Figure 6B shows the peak fitting results of the H₂-TPR profiles in the rectangle area. All reduction peaks were deconvoluted into four groups of sub-bands with the correlation coefficients (r^2) above 0.99 and named as T₁, T₂, T₃, and T₄ from low to high temperatures. The T₁ sub-bands are attributed to the reduction process of surface oxygen and the T_2-T_4 subbands are attributed to the reduction processes of lattice oxygen. It seemed that the amounts of surface oxygen derived from the H₂-TPR data on these samples were different from those derived from the O 1s XPS data to a certain extent, probably because of the discrepancy in precision between different characterization techniques with distinct experimental conditions. For the T_2-T_4 sub-bands, more specifically, the $T_2\ \text{sub-bands}$ are due to the reduction of Fe^{3+} to $Fe^{(3-\delta)+}$ with intermediate valence as that in Fe₃O₄. For the standard reduction process from Fe³⁺ to $Fe^{(3-\delta)+}$ and then to Fe^{2+} , the area ratio of the two H_2 consumption peaks should be 1:2. From $Fe_1Ti_4O_x$ to $Fe_4Ti_4O_x$, the $T_2/(T_3 + T_4)$ ratios are below 1:2 as shown in the right side of Figure 6B, indicating that partial Fe²⁺ species have been indeed reduced to Fe^0 in the T₃ and T₄ processes. For $Fe_4Ti_2O_x$



Figure 7. In situ DRIFTS results of (A) NH₃ and (B) NO + O₂ adsorption on Fe_aTi_bO_x serial catalysts at 150 °C. (C) Deconvoluted results of bands attributed to nitrate species. (D) Correlation between NO_x conversion in NH₃-SCR reaction at 150 °C and amounts of relevant nitrate species.

and Fe₄Ti₁O_x, the T₂/(T₃ + T₄) ratios are above 1:2, revealing that partial iron species is still in the intermediate valence Fe^{(3- δ)+} after reduction below 500 °C, mainly due to the formation of aggregated Fe₂O₃ particles in original catalysts. As for pristine Fe₂O₃, the T₂-T₄ sub-bands could be totally ascribed to the reduction from Fe₂O₃ to Fe₃O₄, possibly at different oxide layers. These results are in well accordance with the conclusions that we draw from the H₂/Fe ratios above.

Correlation between Catalytic Performance and Reactant Adsorption Capability/Conformation. The apparent SCR activity of catalysts usually correlates with the adsorption amounts of NH₃ and NO_x, especially in the low temperature range where the SCR reaction mainly follows a Langmuir— Hinshelwood (L-H) mechanism between NH₃ and NO_x adsorbed species.³⁴ Therefore, the correlation between catalytic performance and reactant adsorption capability/conformation over iron titanate catalysts was studied in detail using in situ DRIFTS method to detect the surface species and TPD method to measure the total adsorption amounts.

In Situ DRIFTS of NH₃ and NO + O₂ Adsorption. Figure 7A shows the results of in situ DRIFTS of NH₃ adsorption on Fe_aTi_bO_x serial catalysts at 150 °C. After NH₃ adsorption and N₂ purge, the sample surfaces were mainly covered by ionic NH₄⁺ (δ_s at 1684 cm⁻¹ and δ_{as} at 1429–1444 cm⁻¹) bound to Brønsted acid sites³⁵ and coordinated NH₃ (δ_{as} at 1599–1605 cm⁻¹ and δ_s at 1186–1201 cm⁻¹) bound to Lewis acid sites.³⁶ The negative

bands around 1370 cm⁻¹ $(\nu_{(as)S=O})^{36,37}$ on titanium-containing samples are attributed to the coverage of sulfate species by NH₃, which was the residue from Ti(SO₄)₂ precursor during the preparation procedures. Comparing with the NH3 adsorbed species on pristine TiO_2 , the adsorption amounts of both ionic NH_4^+ and coordinated NH₃ on iron titanate catalysts showed obvious increase, due to the formation of larger surface area and larger amounts of acid sites through interaction between iron and titanium species. On Fe₄Ti₂O_x and Fe₄Ti₁O_x with the Fe–Ti molar ratios exceeding 1:1, the band intensities of NH₃ adsorbed species showed slight decrease compared with that over Fe₄Ti₄O_x, mainly due to the formation of aggregated Fe₂O₃ particles. As expected for pristine Fe₂O₃, the adsorption amount of NH₃ was rather small. The appearance of the shoulder peak at 1151 cm⁻¹ attributed to NH₂ rocking vibration mode³⁸ implies that in the high temperature range where the SCR reaction mainly follows an Eley-Rideal (E-R) mechanism between NH₂ and gaseous NO, the H-abstraction reaction of NH₃ is mainly completed over iron sites, which is in well accordance with the conclusion that we have drawn in our previous study.³⁴ This result also suggests that the deep dehydrogenation effect would occur over iron titanate catalysts in the hightemperature range when the Fe amount is too large, resulting in the occurrence of unselective oxidation of NH3 and thus the decrease of NO_x conversion.

Although the adsorption amounts of NH_3 on $Fe_4Ti_2O_x$ and $Fe_4Ti_1O_x$ showed a slight decrease compared with that on $Fe_4Ti_4O_x$ as shown in Figure 7A, the apparent NO_x conversions on these two samples in Figure 1 still showed some increase, especially in the low temperature range below 200 °C. Therefore, the amounts of NH₃ adsorbed species over all iron titanate catalysts should be totally enough for the real SCR reaction, and the amounts of NO_x adsorbed species should be crucial for the difference of apparent SCR activities. Accordingly, the in situ DRIFTS of NO + O₂ adsorption on Fe_aTi_bO_x serial catalysts at 150 °C were also conducted, and the results are shown in Figure 7B. After NO + O₂ adsorption and N₂ purge, the sample surfaces were mainly covered by three kinds of nitrates, including monodentate nitrate (ν_3 high vibration mode at 1545–1558 cm⁻¹), bidentate nitrate (ν_3 high vibration mode at 1579 cm⁻¹),^{39–41} and bridging nitrate (ν_3 high vibration mode at 1603–1628 cm⁻¹ and ν_3 low vibration mode at 1211-1232 cm⁻¹).^{41,42} With the increase of Fe amount from pristine TiO_2 to $Fe_4Ti_1O_r$, the NO_r adsorption amounts showed an obvious increase and the relative proportions of these three kinds of nitrates also showed variation. Over pristine Fe2O3, the NO_x adsorption amount returned to be rather low, probably due to the small surface area of this sample. By the way, the band at 1281 cm⁻¹ assigned to the ν_3 low vibration mode of monodentate nitrate (which was possibly overlapped by v_3 low vibration mode of bridging nitrate over other samples) was also observed over Fe_2O_3 , indicating that NO_x can be effectively adsorbed in the form of monodentate nitrate over iron oxide.

Our previous study showed that the reactivity of monodentate nitrate in the SCR reaction was much higher than that of bridging nitrate on iron titanate catalyst, and the bridging nitrate could not form if the titanium sites were pre-covered by NH₃ species; once formed on the surface, the bidentate nitrate was inactive to be reduced, just as the spectator species in the SCR reaction.³⁴ In this study, we can correlate the amounts of these three kinds of nitrates with the apparent NO_x conversions over Fe_aTi_bO_x serial catalysts to further confirm this point of view, which can also provide guidance for catalyst design in the future if we want to further enhance the low temperature activity. Therefore, the ν_3 high vibration modes of nitrate species on Fe_aTi_bO_x serial catalysts are deconvoluted into several groups of sub-bands with the correlation



Figure 8. (A) NH₃-TPD, (B) normalized integral areas of NH₃ signals by surface area and (C) NO_x-TPD, (D) normalized integral areas of NO_x signals by surface area on Fe_a Ti_bO_x serial catalysts.

coefficients (r^2) above 0.99 as shown in Figure 7C. The integral areas of monodentate nitrate (centered in the range of 1494-1556 cm^{-1}), bidentate nitrate (centered in the range of 1577–1581 cm^{-1}), and bridging nitrate (centered in the range of $1602-1630 \text{ cm}^{-1}$) are calculated accordingly, which can represent the adsorption amounts of different nitrate species at 150 °C. And then, the NO_x conversions over these samples at 150 °C are depicted in Figure 7D as a function of integral areas of different nitrate species. Evidently, the best fitting degree is obtained between the NO_x conversions and integral areas of monodentate nitrate on Fe₁Ti₄O_x to Fe₄Ti₁O_x catalysts with the correlation coefficients (r^2) being 0.992 (dashed line). The data of pristine TiO_2 and Fe_2O_3 were not on this fitting line, probably because no synergistic effect between iron and titanium species existed in these samples for the SCR reaction. No obvious linear dependence between the NO_x conversions and integral areas of bidentate nitrate and bridging nitrate is observed, indicating that an appropriate method to enhance the low temperature activity is to increase the adsorption amount of monodentate nitrate on the SCR catalysts. The substitution of partial Fe by Mn in iron titanate catalyst is a good example for this conclusion, through which the formation of monodentate nitrate is greatly enhanced and the low temperature activity is also greatly improved.43

NH₃-TPD and NO_x-TPD. The total adsorption capabilities of NH_3 and NO_x over $Fe_aTi_bO_x$ serial catalysts were measured by NH_3 -TPD and NO_x-TPD, respectively. As the NH₃-TPD results show in Figure 8A, the total adsorption amounts of NH₃ on iron titanate catalysts were much larger than those over pristine TiO₂ and Fe₂O₃ because of the larger surface areas and more abundant acid sites due to the strong interaction between iron and titanium species.³⁴ The bands below 150 °C are attributed to the desorption of physisorbed NH₃ and partial ionic NH₄⁺ bound to weak Brønsted acid sites.14,44 The large broad bands from 247 to 356 °C are due to the desorption of ionic NH4⁺ bound to strong Brønsted acid sites and coordinated NH₃ bound to Lewis acid sites.⁴⁵ By comparing the NH₃ desorption amounts over TiO₂ and Fe₂O₃, we can conclude that over iron titanate catalysts the NH₃ species mainly adsorb onto titanium sites in the form of ionic NH4⁺ and coordinated NH₃, both of which can participate into the SCR reaction.³⁴ The normalized integral areas of NH₃ desorption bands by surface area on different samples are shown in Figure 8B. With the increase of Fe content in samples, the NH₃ desorption amounts per surface area showed some decrease to a certain extent, with the lowest desorption amount obtained on pristine Fe₂O₃, This result

means that the excess iron species in $\text{Fe}_a \text{Ti}_b O_x$ serial catalysts are indeed not beneficial to the adsorption of NH₃, which is in well accordance with the in situ DRIFTS results of NH₃ adsorption in Figure 7A.

The NO_x-TPD results are shown in Figure 8C, among which the pristine TiO_2 showed a very small amount of desorbed NO_r . With the increase of Fe amount from $Fe_1Ti_4O_x$ to $Fe_4Ti_1O_x$, the NO_x desorption amounts showed obvious increase. The bands below 100 °C are due to the desorption of physisorbed NO_x, and the bands at 100-130 °C are attributed to the decomposition of monodentate nitrate.³⁴ Bridging nitrate and bidentate nitrate usually show much higher thermal stability, thus the bands located at 353-387 °C are ascribed to the multiple desorption of these two species. Even though the surface area of Fe_2O_3 is very small, the NO_x desorption amount is still rather large, implying that over iron titanate catalysts the NO_x species mainly adsorb on iron sites. The normalized integral areas of NO_x desorption bands by surface area depicted in Figure 8D also clearly show that the NO_x adsorption capability is monotonously enhanced with the increasing of Fe-Ti molar ratios, which is consistent with the results in Figure 7B. Summarizing the NH₃-TPD and NO_x-TPD results we can conclude that both of the iron and titanium species are effective in the reactant adsorption and an appropriate molar ratio of these two species is very crucial for the improvement of SCR activity over iron titanate catalyst. This is another important reason for obtaining the highest TOF in NO_x reduction process over Fe₄Ti₄O_x below 200 °C.

Conclusions

 $Fe_aTi_bO_x$ serial catalysts with different Fe-Ti molar ratios were facilely synthesized using coprecipitation method and tested for the NH₃-SCR of NO_x. With the increase of the Fe amount from $Fe_1Ti_4O_x$ to $Fe_4Ti_1O_x$, the apparent NO_x conversions showed obvious increase at low temperatures, companied with some decrease at high temperatures. Below 200 °C, the highest TOF of NO_x was obtained over $Fe_4Ti_4O_x$ with Fe:Ti = 1:1. Comparing with the pristine TiO₂ and Fe₂O₃, the coexistence of iron and titanium species in iron titanate catalysts could lead to larger surface area and pore volume, smaller particle size, enhanced oxidative ability of Fe³⁺, and more abundant acid sites over catalyst surface. Due to the strong adsorption of NH₃ on the iron titanate catalyst surface, the apparent NO_x conversions at low temperatures mainly correlated well with the NO_x adsorption amounts, especially the monodentate nitrate amounts. The excess iron species in $Fe_4Ti_2O_x$ and $Fe_4Ti_1O_x$ in the form of small Fe_2O_3 particles was favorable to the formation of monodentate nitrate at low temperatures; therefore the apparent NO_x conversions were enhanced on these two samples. However, the deep dehydrogenation and unselective oxidation of NH₃ would occur over Fe₂O₃ particles at high temperatures, thereby leading to a decrease of apparent NO_x conversions and N2 selectivity. An appropriate proportion of iron and titanium species is very important to balance the SCR activity and N₂ selectivity over iron titanate catalysts.

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Supporting Information Available: N₂ selectivity as a function of temperature in the NH₃-SCR reaction over Fe_aTi_bO_x serial catalysts (Figure S1) and UV–vis DRS results of Fe_aTi_bO_x serial catalysts (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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