Strong metal–support interaction of Ru on TiO$_2$ derived from the co-reduction mechanism of Ru$_x$Ti$_{1-x}$O$_2$ interphase

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Article

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Abstract

Strong metal–support interaction (SMSI) plays a crucial role in determining the catalytic performances of supported metal catalysts, in which the subsequent migration of supports over the pre-existing metal nanoparticles is generally considered during the pretreatment condition. Herein, a distinct mechanism of SMSI generation by the co-reduction of oxide interphase is addressed over the Ru/TiO$_2$ catalysts. Our results demonstrate that the formation of Ru$_x$Ti$_{1-x}$O$_2$ oxide interphase can be facilely augmented by increasing the calcination temperature over Ru/TiO$_2$ catalysts, while a growing encapsulation of TiO$_x$ overlayer on metallic Ru nanoparticles can be acquired in the following reduction of this oxide interphase. In contrast, the SMSI generation by the conventional mechanism is highly suppressed over the RuO$_2$/TiO$_2$ phase calcined at a low temperature. Thanks to this improved SMSI on Ru/TiO$_2$ catalyst, it thus possesses an excellent performance in CO$_2$ methanation, with a promoted CO$_2$ conversion activity. Our findings suggest a different mechanism for the SMSI generation through the oxide interphase formation, and it also offers an alternative pathway to tune catalytic properties of supported metal catalysts.

Introduction

The strong metal–support interaction (SMSI) was first discovered by Tauster et al. to describe the phenomenon that reducible oxides supported group VIII noble metals suffer a significant suppression of CO and H$_2$ chemisorption after high-temperature reduction treatment$^{1,2,3,4}$ Generally, the pre-existing metal nanoparticles on the supports was suggested during the processes of SMSI, on which the subsequent migration of supports occurs over metal nanoparticles in a reduction condition which is regarded as the classical formation mechanism of SMSI. For decades, researchers have devoted their efforts to exploring the other possible pathways for SMSI formation, in which extensive mechanisms, including the oxidative SMSI$^{5,6,7}$ adsorbate-mediated SMSI$^{8}$ reaction-induced SMSI$^{9,10}$ and carbonization-induced SMSI$^{11}$ have been developed so far in terms of the varied formation conditions for the migration of supports over metal nanoparticles.

According to the classical formation mechanism, the SMSI generation was greatly reliable to the preferable reducibility of metal oxide. However, due to the chemical interactions of metal oxide with the supports which is also oxide in many cases, the formation of solid solution of oxide interphase would encounter during the pretreatment of precursors in the practical synthesis of metals on the supports, which makes the stepwise reduction of metal oxides to metallic nanoparticles on support a challenge. In this case, the mechanism of SMSI generation would differ from the classical SMSI. More recently, the researches have also demonstrated that the migration of support components is greatly sensitive to the contact interface between metal and support in an SMSI system$^{12,13}$ while a mechanistic understanding for the role of reduction mechanism in this state of SMSI formation is still lacking.

Herein we have focused on the effect of virgin catalyst states on SMSI formation in the Ru/TiO$_2$ catalytic system. Benefiting from the similar crystal parameters between RuO$_2$ and rutile TiO$_2$, an epitaxial growth
of RuO$_2$ on rutile TiO$_2$ can be observed after calcination treatment on the Ru/TiO$_2$ catalyst, which results in the formation of a Ru$_x$Ti$_{1-x}$O$_2$ interphase between RuO$_2$ and rutile TiO$_2$. With increasing the pre-calcination temperature of Ru/TiO$_2$ catalysts, the Ru$_x$Ti$_{1-x}$O$_2$ interphase with the Ru$\text O$–Ti bonding can be effectively augmented. More importantly, it leads to an enhanced TiO$_x$ overlayer on Ru nanoparticles, through a co-reduction of Ru and Ti in the Ru$\text O$–Ti bonds in the $H_2$ reduction treatment. It thus demonstrates that the formation of SMSI by the co-reduction mechanism becomes predominant than the classical one in this Ru/TiO$_2$ catalyst. Considering that the SMSI of metal/support catalysts has played a key role in heterogeneous catalysis which has attracted worldwide interest, especially in CO/CO$_2$ hydrogenation reactions, for which the catalytic CO$_2$ methanation is taken as a prototype reaction to probe the SMSI effect of Ru/TiO$_2$ catalyst. Thanks to this improved SMSI on Ru/TiO$_2$, it thus possesses an excellent performance in CO$_2$ methanation, with a promoted CO$_2$ conversion activity. This work provides an additional formation mechanism of SMSI and offers an opportunity to tailoring the catalytic performance by SMSI.

**Results**

The Ru/TiO$_2$ catalysts in this work were obtained with a wet impregnation method by loading the RuCl$_3$ precursor onto a rutile-type TiO$_2$, followed by calcination in air at different temperatures to acquire a varied chemical interaction between RuO$_2$ and rutile TiO$_2$. The resulting samples after calcination and a chlorides removal process are denoted as Ru/TiO$_2$-xAir, where x indicates the intended calcination temperature (200, 300, 400, or 500°C). The loading of Ru in the Ru/TiO$_2$-xAir is 2.25 wt% as determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES).

**Structure Identification.** All the Ru/TiO$_2$-xAir samples possess similar surface areas and pore volumes as indicated by N$_2$ physisorption (Table S1). The X-ray diffraction (XRD) patterns of the Ru/TiO$_2$-xAir samples do not show any diffraction associated with Ru or RuO$_2$ species (Figure S1), suggesting the high dispersion of Ru species on the rutile TiO$_2$ after calcination, which is further confirmed by the highly dispersed Ru/Ti/O in the elemental mapping results (Figure S2).

As rutile TiO$_2$ and RuO$_2$ own the same crystal space group with comparable lattice parameters (Table S2), the calcination treatment of Ru/TiO$_2$ is expected to trigger a chemical solid solution between RuO$_2$ and rutile TiO$_2$, which is then investigated by various characterizations. As shown in Fig. 1a, the Raman spectrum of the TiO$_2$ support shows characteristic bands of the rutile phase at 447 ($E_g$) and 612 cm$^{-1}$ ($A_{1g}$). After the incorporation with RuO$_2$, a new band associated with RuO$_2$ appeared at $\sim$ 500 cm$^{-1}$, suggesting the presence of RuO$_2$ species in the Ru/TiO$_2$-xAir samples. The $E_g$ bands show a red shift of $\sim$ 30 cm$^{-1}$ after the calcination treatments, which indicates the formation of Ru$_x$Ti$_{1-x}$O$_2$ interphase (Ru$\text O$–Ti bonding) between RuO$_2$ and rutile TiO$_2$. With increasing the calcination temperature, the shift of $E_g$ bands from 420 to 414 cm$^{-1}$ can be originated from the increased proportion of Ru$_x$Ti$_{1-x}$O$_2$ interphase
in the Ru/TiO$_2$-xAir system. According to the high-resolution transmission electron microscopy (HRTEM) observations in Figure S3, distinct morphologies of the supported Ru species are observed. The Ru/TiO$_2$-200Air sample possesses dominant RuO$_2$ nanoparticles (NPs) with clear boundaries on TiO$_2$ support. In contrast, for the Ru/TiO$_2$-xAir (x = 300, 400, or 500°C) samples, the supported RuO$_2$ NPs can hardly be clearly identified, which implies the proceeding epitaxial growth of RuO$_2$ on the rutile TiO$_2$ support to form Ru$_x$Ti$_{1-x}$O$_2$ interphase after high temperature calcination.

The structure evolution of the Ru/TiO$_2$-xAir samples is further explored by the X-ray absorption spectroscopy (XAS). The X-ray absorption near-edge structure (XANES) results indicate that Ru$^{4+}$ species is dominant in all the Ru/TiO$_2$-xAir samples as their edge energies are found to be similar with that of RuO$_2$ (Figure S4). From the extended X-ray absorption fine structure (EXAFS) and the fitting results in Fig. 1b and Table S3, increasing the calcination temperature leads to a progressive increase in the coordination number (CN) of Ru–O (~ 1.98 Å) and that of Ru–Ru$_2$ (~ 3.59 Å). While similar CNs of Ru–Ru$_1$ in the second shell are observed with a low value of 0.3 ~ 0.5 for all the Ru/TiO$_2$-xAir samples. These findings suggest the facile formation of large but flat RuO$_2$ islands on TiO$_2$ during the calcination treatment as illustrated in Fig. 1c. In addition, the Ru/TiO$_2$-xAir samples present an extra coordination environment of Ru–O–Ti bonding (~ 3.00 Å), suggesting the formation of Ru$_x$Ti$_{1-x}$O$_2$ interphase. The Ru/TiO$_2$-200Air sample possesses a low coordinated Ru–O–Ti with a CN of only 0.2, indicative of the dominant RuO$_2$ NPs in the Ru/TiO$_2$-200Air catalyst. With increasing the calcination temperature from 300 to 500°C, the CN associated with Ru–O–Ti slightly increases from 0.7 to 0.9, which demonstrates the enhancement of Ru$_x$Ti$_{1-x}$O$_2$ interphase as shown in the white boxes of Fig. 1c. This finding is also in good agreement with that of Raman spectra and TEM observations.

**SMSI formation.** As reported previously,$^{22,23,24}$ a high-temperature reduction treatment of Ru/TiO$_2$ leads to the SMSI of TiO$_x$ overlayer encapsulation over the Ru NPs. To investigate the role of Ru$_x$Ti$_{1-x}$O$_2$ interphase in SMSI mechanism in Ru/TiO$_x$ catalysts, all Ru/TiO$_2$-xAir samples were then reduced with H$_2$ at 450°C which were referred as Ru/TiO$_2$-xAir-R. As observed by TEM images (Figures S5), the morphologies of the Ru/TiO$_2$-xAir-R catalysts exhibit a slight aggregation of Ru NPs as the pre-calcination temperature increases. However, no diffraction peak related with Ru species appears in XRD patterns of the Ru/TiO$_2$-xAir-R catalysts (Figures S6), which indicates the formation of flat Ru species on TiO$_2$ surface as illustrated above in Fig. 1c. The variation of Ru chemical states was then determined by XAS experiments. The XANES spectra of the Ru/TiO$_2$-xAir-R catalysts show a shift of Ru K-edge to Ru foil as the pre-calcination temperature increases (Fig. 2a), indicative of an increasing reduction degree of Ru NPs which might be caused by the Ru size enlargement. Confirming from the EXAFS of Ru K-edge and the corresponding fitting results (Figure S7 and Table S4), the CN of Ru–Ru pair (~ 2.67 Å) from 2.8 to 7.5 shows an increase with improving the pre-calcination temperature in the Ru/TiO$_2$-xAir-R catalysts. The
HRTEM images in Fig. 2b then reveal that Ru NPs tend to be encapsulated by TiO$_x$ overlayer at a pre-calcination temperature higher than 300°C. With increasing the pre-calcination temperature of the Ru/TiO$_2$-$x$Air-R catalysts, an obvious decrease of CO chemisorption is observed (Figure S8 and Table S5), which in turn indicates the growth of TiO$_x$ overlayer as observed in the HRTEM images.

Diffuse reflectance infrared Fourier transform spectra of CO (CO-DRIFTS) were used to probe the structure evolution of the Ru/TiO$_2$-$x$Air-R catalysts. As shown in Fig. 2c, there are three distinct models associated with CO adsorption on the Ru NPs over the Ru/TiO$_2$-$x$Air-R catalysts. The band at 2030 ~ 2050 cm$^{-1}$ is assigned to linear CO adsorption on metallic Ru NPs, while the bands at 2136 and 2075 cm$^{-1}$ are related to CO adsorption on partially oxidized Ru$^{n+}$ species. An enhanced proportion of the metallic Ru was observed with the increase of the pre-calcination temperature, which indicates the improvement of Ru reduction as observed by XAS results. The weakened intensity of CO adsorption together with the red shift of bands related to metallic Ru implied the decreased CO coverage, which in turn demonstrated the growing encapsulation of TiO$_x$ overlayer on Ru NPs with increasing the pre-calcination temperature. Therefore, a high pre-calcination temperature is in favor of the reduction of Ru/TiO$_2$ and the following formation of SMSI in the Ru/TiO$_2$-$x$Air-R catalysts. In combination with the structural behaviors of the Ru/TiO$_2$-$x$Air catalysts, the formation of Ru–O–Ti bonding in the Ru$_x$Ti$_{1-x}$O$_2$ interphase is bound to play a vital role in the facile formation of SMSI during a reduction treatment at 450°C.

**SMSI Formation Mechanism.** The reduction behaviors of the Ru/TiO$_2$-$x$Air samples were then explored with H$_2$-TPR experiments to give a mechanistic understanding of SMSI generation. As shown in Fig. 3a, the Ru/TiO$_2$-$200$Air sample exhibits two main reduction peaks (at 65 and 514°C), which are assigned to the reduction of RuO$_2$ NPs and the TiO$_2$ substrate, respectively. In terms of the reduction temperature of 450°C in our sample pretreatment, the Ru/TiO$_2$-$200$Air sample suffers predominantly the reduction of RuO$_2$ to metallic Ru phase, while the reduction of TiO$_2$ to form TiO$_x$ overlayer can hardly occur. As a result, rare SMSI state is observed over the Ru/TiO$_2$-$200$Air-R sample, which indicates that the formation of SMSI in the Ru/TiO$_2$-$200$Air-R sample would follow the conventional SMSI mechanism as depicted in Fig. 3b. Namely, metallic Ru NPs can be facilely acquired at a low reduction temperature, while the migration of TiO$_x$ overlayer on Ru surface needs a high-temperature reduction treatment due to the relatively inert TiO$_2$ substrate.

In contrast, the Ru/TiO$_2$-$x$Air ($x$ = 300, 400 or 500°C) samples mainly show one compound reduction peak at ~ 150°C, and their H$_2$ consumption is about 1.5 times as the theoretical estimation from RuO$_2$ reduction (Table S6), which indicates the co-reduction of both RuO$_2$ and TiO$_2$ species, primarily due to the presence of Ru$_x$Ti$_{1-x}$O$_2$ interphase. In these cases, the reduction of TiO$_2$ species becomes facile, which subsequently facilitates the formation of SMSI states. According to the above observations, we have proposed a co-reduction mechanism for the formation of SMSI in the Ru/TiO$_2$-$x$Air ($x$ = 300, 400 or 500°C) systems as illustrated in Fig. 3c. By the high-temperature calcination treatment of Ru/TiO$_2$, the RuO$_2$
proceeds an epitaxial growth on the rutile TiO$_2$ support to form Ru$_x$Ti$_{1-x}$O$_2$ interphase. Benefiting from the presence of Ru–O–Ti bonding in the Ru$_x$Ti$_{1-x}$O$_2$ interphase, the co-reduction of Ru and Ti can be greatly facilitated upon H$_2$ treatment, which leads to an enhancement of TiO$_x$ overlayer on Ru NPs consequently. Therefore, we can speculate that a low-temperature reduction treatment of the Ru/TiO$_2$-xAir (x ≥ 300°C) can also lead to SMSI due to facile co-reduction of Ru$_x$Ti$_{1-x}$O$_2$ interphase.

**CO$_2$ Methanation.** The methanation of CO$_2$, known as the Sabatier reaction, is usually promoted by a moderate SMSI.$^{33,34,35}$ With increasing the pre-calcination temperature of Ru/TiO$_2$ from 200 to 500°C, an enhanced SMSI can be acquired for the Ru/TiO$_2$-xAir samples reduced at 300°C (Ru/TiO$_2$-xAir-300R catalysts) as reflected by the gradually decreasing CO chemisorption (Table S7). The SMSI acquired by the co-reduction mechanism then provides an effective approach to tuning the catalytic performance of CO$_2$ methanation. As shown in Fig. 4a and Table S8, all the Ru/TiO$_2$-xAir-300R catalysts exhibit 100% CH$_4$ selectivity, with the intrinsic activity (reflected as TOF) soaring with increasing the pre-calcination temperature, which benefits from the growing tendency to SMSI generation. In contrast, the Ru/TiO$_2$-200Air-300R catalyst exhibits a much lower TOF value for the absence of SMSI.

For the Ru/TiO$_2$-200Air sample, a high-temperature treatment can also lead to a SMSI state similar with the case of classical migration mechanism for SMSI formation. As shown in Fig. 4b, the activity of CO$_2$ methanation is greatly improved with increasing the reduction temperature from 300 to 600°C, which suggests that the formation of an appropriate SMSI in the Ru/TiO$_2$ system can greatly promote the performance of CO$_2$ methanation.

To give a better comparison, we have also fabricated a Ru/TiO$_2$-300N sample which was calcined in a N$_2$ atmosphere instead of air to avoid the generation of Ru$_x$Ti$_{1-x}$O$_2$ interphase. As expected, the reduction of TiO$_2$ in the Ru/TiO$_2$-300N sample required a temperature higher than 400°C as reflected by the H$_2$-TPR result (Figure S9). With increasing the reduction temperature from 300 to 600°C, an enhanced activity of CO$_2$ methanation is also observed for the Ru/TiO$_2$-300N samples (Fig. 4b and entries 7–9 in Table S8), confirming of the promotional effect of SMSI on the performance of CO$_2$ methanation. The activity of the Ru/TiO$_2$-500Air-300R catalyst is 1.9 and 5.5 times as that of the Ru/TiO$_2$-200Air-600R and Ru/TiO$_2$-300N-600R, respectively. It thus further demonstrates the enhanced formation of SMSI by a co-reduction mechanism of the Ru$_x$Ti$_{1-x}$O$_2$ interphase than the classical migration mechanism on the Ru/TiO$_2$ catalysts.

**Conclusion**

In conclusion, the evolution of Ru/TiO$_2$ catalyst is intensively studied to address the derivation of strong metal-support interaction by varying the calcination temperature. A high calcination temperature treatment favors the formation of extensive Ru–O–Ti bonding in the Ru$_x$Ti$_{1-x}$O$_2$ interphase, which promotes the co-reduction of Ru and Ti upon H$_2$ reduction treatment. The facile reduction of TiO$_2$ species
further leads to an enhancement of migrated TiO$_x$ overlayer. The SMSI can be more easily acquired by the co-reduction mechanism compared with the classical migration mechanism as reflected by the promoted performance of CO$_2$ methanation. This work gives a new understanding of the SMSI generation mechanism and provides an effective approach to tailoring catalytic properties by SMSI.

**Methods**

**Synthesis of the Ru/TiO$_2$-x Air samples.** Typically, 1.75 g of the ruthenium (III) chloride was diluted with pure water to 50 mL, followed by adding 2.0 g of rutile TiO$_2$ to the solution with vigorous stirring. Then, the suspension was dried in a 50°C water bath through evaporation, followed by drying at 110°C. The obtained solid was denoted as Ru/TiO$_2$-dried, which was following calcination in air at an intended temperature (200, 300, 400 or 500°C) for 3 h. Then, a dilute ammonia solution was used to wash the sample repeatedly in order to remove the residual chlorides. The sample after an overnight drying at 60°C was then denoted as Ru/TiO$_2$-xAir, where x indicates the intended calcination temperature (200, 300, 400 or 500°C). The Ru loading in the Ru/TiO$_2$-xAir catalyst is 2.25 wt% as detected by ICP-OES.

**Synthesis of the Ru/TiO$_2$-300N sample.** The Ru/TiO$_2$-300N sample was acquired by calcining the Ru/TiO$_2$-dried in a nitrogen flow at 300°C, followed by the same chlorides removal treatment as that for acquiring the Ru/TiO$_2$-xAir samples. The Ru loading in the Ru/TiO$_2$-300N catalyst is 2.32 wt% as detected by ICP-OES.

The Ru/TiO$_2$ samples reduced with H$_2$ at a desired temperature (X = 300, 450 or 600) were then denoted as Ru/TiO$_2$-xAir-XR or Ru/TiO$_2$-300N-XR catalysts. Unless stated, the Ru/TiO$_2$-xAir-450R appears in the form of Ru/TiO$_2$-xAir-R.

**Characterization.** The Ru loadings were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an ICP-OES 7300DV instrument. Powder X-ray diffraction (XRD) data were recorded using a PANalytical X’Pert-Pro X-ray diffractometer with Cu Kα radiation source (λ = 0.15432 nm). Nitrogen adsorption-desorption isotherm was performed with a Micromeritics ASAP 2460 instrument at −196°C. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), elemental mapping, and high-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL JEM-2100F microscope operating at 200 kV. Raman spectra were recorded with a dispersive Horiva Jobin Yvon LabRam HR800 microscope equipped with a He-Ne laser (633 nm).

X-ray absorption spectroscopy (XAS) data at the Ru K-edge, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES), were acquired at the BL 14W1 of Shanghai Synchrotron Radiation Facility (SSRF), China. The Ru/TiO$_2$-xAir sample was squashed into a wafer in air and sealed with Capton film, while the Ru/TiO$_2$-xAir-R sample was first pretreated with H$_2$ at 450°C for 2 h, followed by sealing with Capton film in a glove box. The spectrum was collected in the transmission mode, following which the acquired data were analyzed with the Athena software package.
Diffuse reflectance infrared Fourier transform spectrum (DRIFTS) was recorded on a Bruker Equinox 55 spectrometer. For each CO adsorption, the sample was in situ pretreated with H\textsubscript{2} for 1 h at 450°C, followed by cooling down to 25°C. The gas flow was then switched to He and held for 0.5 h, following which the background spectrum was collected. Then, a 5 vol% CO/He was introduced into the system until achieving a saturated adsorption of CO. Subsequently, the system was purged with He to remove gaseous CO, following which the DRIFT spectrum of CO adsorption was collected.

CO chemisorption was employed with a Micromeritics AutoChem II 2920 instrument. The sample was pretreated with H\textsubscript{2} for 1 h at a designed temperature, followed by purging with He for 0.5 h to remove surface adsorbed H species. Then, the sample was cooled down to 50°C, and a 5 vol% CO/He was repeatedly injected into the reactor until acquiring a saturated CO adsorption. CO microcalorimetric measurements were conducted at 40°C using a BT 2.15 Calvet calorimeter which is equipped with MKS 698A Baratron capacitance manometers. The sample was pretreated with H\textsubscript{2} for 1 h at 450°C, followed by evacuation at 460°C for 0.5 h. After cooling down to room temperature, the quartz tube was tightly sealed followed by transferring to the calorimetric cell and outgassing at 40°C overnight. Then, CO microcalorimetry was carried out during the stepwise import of CO at 40°C.

H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) was also conducted with a Micromeritics AutoChem II 2920 apparatus. The sample was pretreated with Ar for 1 h at 200°C, followed by cooling down to 50°C. Then, a 10 vol% H\textsubscript{2}/Ar was introduced into the system by heating the sample from 50 to 800°C.

**CO\textsubscript{2} hydrogenation.** CO\textsubscript{2} hydrogenation tests were performed in a fixed-bed quartz reactor with an inner diameter of 10 mm. Typically, 0.1 g of Ru/TiO\textsubscript{2} catalyst was diluted with 1.0 g of quartz sand and then loaded into the reactor. Prior to catalytic testing, the sample was in situ reduced with H\textsubscript{2} for 2 h at a designed temperature, followed by cooling down to the reaction temperature. Then, the feed gas (H\textsubscript{2}/CO\textsubscript{2}/N\textsubscript{2} = 70/20/10 (v/v/v)) was introduced into the reactor for CO\textsubscript{2} hydrogenation tests, in which N\textsubscript{2} was used as an internal standard. The tests were carried out at 200°C, 0.1 MPa and 60,000 mL g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}.

After passing through an ice-bath (0°C), the gaseous components were analyzed online with an A90 Echrom gas chromatograph which was equipped with a TDX-01 column connected to a thermal conductivity detector (TCD).

**Declarations**

**Data availability**

The data that support the plots within this study are available from the corresponding author on reasonable request.

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Competing interests

The authors declare no competing financial interests.

References


**Figures**

**Figure 1**

Structure evolution of the Ru/TiO₂-xAir catalysts. (a) Raman spectra of rutile TiO₂, Ru/TiO₂-dried, and the Ru/TiO₂-xAir catalysts. (b) Fourier transforms of the k3-weighted EXAFS spectra of Ru K-edge for Ru foil, RuO₂, and the Ru/TiO₂-xAir catalysts, respectively. (c) A schematic illustration of the structural evolution of Ru/TiO₂-xAir catalysts as the calcination temperature varied from 200 to 500 °C.
Figure 2

Structure identification of the Ru/TiO2-xAir catalysts after 450 °C reduction (Ru/TiO2-xAir-R samples). (a) Normalized XANES spectra at the Ru K-edge for Ru foil, RuO2, and the Ru/TiO2-xAir-R catalysts. (b) HRTEM images of the Ru/TiO2-xAir-R catalysts. (c) In situ DRIFT spectra obtained after CO adsorption and evacuation with helium at room temperature (25 °C), over the Ru/TiO2-xAir-R catalysts.

Figure 3

(a) H2-TPR profiles of the Ru/TiO2-xAir catalysts as well as the TiO2 support. (b) A classical support migration mechanism for SMSI formation, as in the case of the Ru/TiO2-200Air sample. (c) A proposed
Ru–O–Ti co-reduction mechanism for facile formation of SMSI, as in the cases of the Ru/TiO2-xAir (x = 300, 400 or 500 °C) samples.

**Figure 4**

(a) Catalytic performance of the series Ru/TiO2-xAir-300R catalysts for CO2 methanation. (b) Catalytic performance for CO2 methanation over the Ru/TiO2-200Air and Ru/TiO2-300N catalysts pretreated at different temperatures. Reaction conditions: 0.1 MPa, 200 °C, space velocity = 60000 mL h−1 gcat−1, H2/CO2/N2 = 70/20/10.

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