

Reactive behaviors of iron-based shift catalyst promoted by ceria

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Received 9 December 1999; received in revised form 14 January 2000; accepted 21 January 2000

Abstract

The reductive behavior of iron-based shift catalyst promoted by cerium oxide was investigated by temperature-programmed reduction (TPR). Two reduction peaks appeared, centered at 473 and 673 K in reduction gas mixtures. The peaks illustrated that the reduced surface states were different, corresponding the reductive temperatures. The optimum reductive temperature range is from 423 to 723 K for the catalyst. The results of temperature-programmed desorption (TPD) and pulse reaction indicated that the mechanism of the water–gas shift reaction on the catalyst can be considered as a redox process. The reduced Fe–Ce–Cr–O can be oxidized by water and carbon dioxide at reaction temperatures (from 573 to 673 K). Water is decomposed to form hydrogen and adsorbed hydroxyl groups, and carbon monoxide reacts with hydroxyl groups to produce hydrogen and carbon dioxide simultaneously. FT-IR spectroscopy results showed that iron-based catalyst promoted by CeO₂ is a structurally sensitive catalyst. It has excellent activity, selectivity, and stability under reaction conditions. Moreover, on the catalyst surface carbonate-like species were not found under reaction conditions, as established by IR spectra. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Water–gas shift reaction; Temperature-programmed reaction; Temperature-programmed desorption; Ceria

1. Introduction

In recent years, high temperature shift catalysts have received considerable attention. The classic iron and chromium-based high temperature shift catalysts possess some problems when used in industrial plant. As is well known, chromium oxide is one kind of poison. At low steam-to-carbon (S/C) ratio it catalyzes the formation of hydrocarbon and oxygenate, which causes a hydrogen loss, deactivation of low temperature shift catalyst, and thereby production loss. It is, therefore, necessary to improve the composition of the classic catalyst and find a new and effective promoter. CeO₂ is known to store and release oxygen and hydrogen, form surface and bulk vacancies, and form intermetallic M–Ce compounds [1]. Accordingly CeO₂ can be used as promoter in combination with other elements to give mixed-oxide formulations. A new kind of iron-based shift catalyst promoted by CeO₂ has been widely used in ammonia synthesis plants, but a more detail understanding on how the materials, including iron oxide, ferric oxide, and CeO₂ in the catalyst, influence the catalytic process is a matter of considerable debate [2–7]. X. Zhang and Klábunde [8] proposed a mechanism in which CO is activated on Cu, with oxygen activated as superoxide O₂ on

the CeO₂ surface, and then transferred to CO. Schlatter and Mitchell [9] proposed that the water–gas shift reaction (WGSR) mechanism could account for the enhanced transient CO conversion they observed following a change from lean to rich conditions on a PM/CeO₂/Al₂O₃ catalyst. They verified that this enhancement was accompanied by formation of equimolar amounts of CO₂ and H₂ during the transient period, and no substantial modification of CO conversion was evidenced in the absence of water. Similar results were obtained by Kim [10] who demonstrated that the transient CO conversion efficiency must be largely due to the water–gas shift reaction, although a contribution from the carbon monoxide and surface oxygen atoms reaction was established, thus accounting also for the oxygen storage capacity of CeO₂. Zafiris and Gorte [11] found evidence that oxygen can migrate from CeO₂ onto deposited Rh particles at relatively low temperature. This oxygen can actually be used to oxidize CO to CO₂; then partially reduced CeO₂ can be reoxidized by water. Most of the mechanisms discussed above refer to exhaust gas conditions.

In this work, we have used temperature-programmed reduction (TPR), in situ Fourier-transform infrared spectrometry, temperature-programmed desorption (TPD), and pulse reaction to investigate iron-based catalyst promoted by CeO₂ (Fe–Ce–Cr–O) in different gas mixtures. The reduction behavior, reaction mechanism and optimum

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reaction conditions have been examined. We attempted to characterize the surface of the catalyst by means of infrared spectroscopy in reaction gases and to investigate the surface state changes under reaction conditions.

2. Experimental

2.1. Catalyst preparation

Iron-based catalyst promoted by ceria was prepared by co-precipitating sulfate salts by NH_4OH at 333 K. Approximately 0.5 mol ferric sulfate, 7 mmol iron sulfate, 7 mmol chromium sulfate, and 23 mmol cerium sulfate were dissolved in 200 cm^3 water. The solution was heated to 333 K and continuously mixed using a mechanical stirrer with adding drop wise aqueous ammonia solution. The precipitate was settled for 2 h, then repeatedly washed with distilled water until no SO_4^{2-} was detected. The precipitate was filtered, 2.5 mmol potassium hydroxide was added, then dried at 383 K overnight. Dried sample was calcined in air at 673 K for 4 h. The specific surface area detected by BET method was $36.6\text{ m}^2/\text{g}$. For comparison, pure Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ (1% Cr_2O_3 and Fe_2O_3) was prepared under the same conditions.

2.2. Apparatus and procedure

TPD and TPR were performed in a gas handling system. The catalyst (0.5 g) was loaded in a U-shape quartz reactor, then reduced in a flowing hydrogen steam mixture (25 mol/min, 50% H_2 in stream) (heating rate 10 K/min) from room temperature to 773 K. A cold trap was placed downstream of the sample to remove any H_2O and CO_2 from the gas before it reached the detector. The hydrogen was monitored using a thermal conductivity detector. The reduced sample was pretreated in nitrogen by heating to 773 K for 30 min in order to remove adsorbate, then cooled down to room temperature. The adsorption was performed at 298 K by pulsing injections of CO_2 or water vapor. Excess CO_2 (or H_2O) was removed in flowing nitrogen until no further desorption of CO_2 (or H_2O) could be detected. The catalyst temperature was ramped at a linear heating rate of 20 K/min in flowing nitrogen (30 ml/min). The gases in the outlet were analyzed by thermal conductivity detector.

The pulse reaction was performed in the same reaction system as above. The reduced sample was pretreated at 773 K for 1 h, then cooled down to 653 K. The reaction on the catalyst was carried out at 653 K by pulse multiple consecutive injections of $\text{CO}/\text{H}_2\text{O}$ mixture. The water and CO_2 in the outlet was cooled down in a cold trap by liquid nitrogen. The components in the outlet were detected by thermal conductivity detector.

Temperature-programmed surface reaction (TPSR) was carried out in a reactor described above. The samples were pretreated at the same conditions as in the TPD experiments.

IR spectra were recorded on a PE-1800 FT-IR spectrometer at $4/\text{cm}$ resolution using a HgCdTe detector. The samples were pressed into a self-supporting disc, weight 30 mg, with a diameter of 10 mm. An IR cell with a internal furnace for heating the disc in situ was connected to a vacuum system which could be kept below 0.0133 N/m^2 . The disc was placed in the IR cell described above, and outgassed at 673 K until surface contaminants were completely removed as indicated by infrared spectroscopy, then it was cooled to room temperature under vacuum (0.0133 N/m^2). In order to obtain Fe_3O_4 active material, a hydrogen/water vapor (1:1) mixture was introduced into the IR cell at 523 K for 2 h, and outgassed at 673 K in order to remove surface adsorbates. Then the sample was cooled down to room temperature in stepwise fashion for recording background spectra from 673 K at intervals of 100 K. The various gases studied were introduced into the IR cell at room temperature. The IR spectra of adsorbed species on the catalyst were collected at the desired temperatures.

3. Results

3.1. Reduction properties

TPR profiles of three catalysts are reported in Fig. 1a. For pure Fe_2O_3 , two peaks were observed at around 483 and 773 K. The low-temperature peak (523 K) was attributed to the reduction of surface oxygen species, while a high-temperature peak (773 K) was attributed to bulk reduction. XRD results showed that the main phase of catalyst at 523 K is $\gamma\text{-Fe}_2\text{O}_3$, and the main phase at 773 K is Fe_3O_4 . More detailed studies were reported elsewhere [20]. Bulk reduction of pure Fe_2O_3 occurred with maximum rate at about 723 K. With composition changes, the reduction properties changed as shown in Fig. 1b and c. The high temperature peaks of Fe–Ce–Cr–O and Fe–Cr–O shifted to

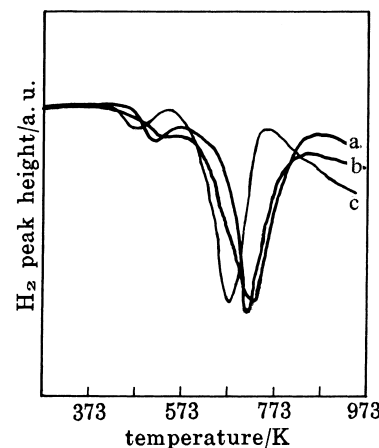


Fig. 1. TPR profile of catalysts. (a) Fe_2O_3 ; (b) Fe–Cr–O and (c) Fe–Ce–Cr–O.

700 and 693 K, separately. XRD studies showed that the main phase in Fe–Cr–O or Fe–Ce–Cr–O under same conditions is all Fe_3O_4 . The reductions of Fe–Ce–Cr–O started at 423 K, i.e., 100 K lower than with pure Fe_2O_3 . So the Fe–Ce–Cr–O catalyst is more easily reduced to Fe_3O_4 than the others. It is obvious that the presence of ceria improves the reducibility of Fe–Ce–Cr–O at low temperatures. This could be attributed to the high oxygen conductivity, due to structural changes introduced by ceria, but the mechanism is not clear. Because the active component in iron-based WGS catalysts is Fe_3O_4 [1], the reduction temperature of Fe–Ce–Cr–O must be below 723 K in order to prevent Fe_3O_4 reduction to Fe. The optimum reduction temperature range of Fe–Ce–Cr–O should be 473–723 K.

3.2. Desorption properties

Fig. 2 shows the traces of CO_2 and H_2O desorbing from Fe–Ce–Cr–O following CO_2 or H_2O adsorption at a linear heating rate of 20 K/min in flowing N_2 (30 ml/min). A H_2O desorption peak and a broad shoulder peak were detected at around 393 and 483 K in Fig. 2a. The H_2O desorption peak at 393 K coincided with the boiling point of water, so it represents the desorption of physically adsorbed water. When being adsorbed on reduced catalyst, some water decomposed to form hydroxyl groups. The TPD profiles suggested that the desorption of hydroxyl groups must occur at high temperatures. At 673 K, there still are some hydroxyl groups that would play an important role in WGS on Fe–Ce–Cr–O.

Three desorption peaks were observed for CO_2 -TPD as shown in Fig. 2b. They represented various of adsorbate species. The desorbing CO_2 at about 323 K was formed by physically adsorbed carbon dioxide. The other two peaks at 423 and 613 K represented the chemisorbed carbon dioxide species on Fe–Ce–Cr–O. IR spectra in Fig. 7 provide evidence that some carbon dioxide forms carbonate species on the catalyst. The carbonate species on the reduced catalyst was difficult to desorb from the surface at low temperatures,

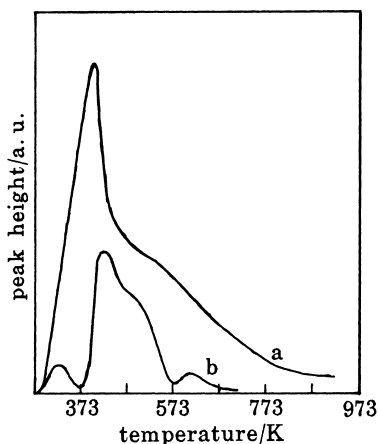


Fig. 2. TPD profile of reduced Fe–Ce–Cr–O₃. (a) H_2O and (b) CO_2 .

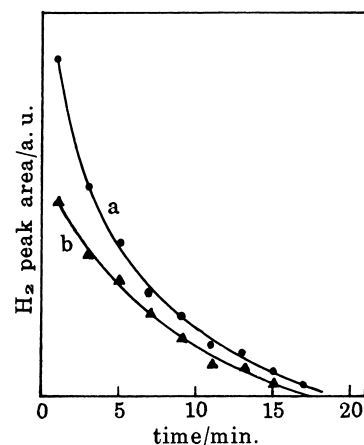


Fig. 3. H_2 output from reaction of H_2O and CO_2 on the reduced Fe–Ce–Cr–O at 653 K. (a) H_2O and (b) CO .

but at temperatures from 573 to 623 K (reaction temperature range) the situation was reversed and most of it desorbed. This is an important feature of the Fe–Ce–Cr–O catalyst.

3.3. Pulse reaction

The 0.5 g of reduced Fe–Ce–Cr–O catalyst was heated to 623 K, then purged with nitrogen with pulse injection of water vapor into the reactor, hydrogen was detected in the outlet, as shown in Fig. 3a. After that, the nitrogen purge was again used until no more hydrogen or other substances were detected, then pulse injection of carbon monoxide occurred. At the outlet, hydrogen was observed again. While water oxidized the surface of the reduced catalyst, adsorbed hydroxyl groups were formed simultaneously. This was verified by IR spectra in Fig. 6. The adsorbed hydroxyl groups can react with carbon monoxide producing both carbon dioxide and hydrogen.

The hydrogen output is related to the amount of active sites on the surface of the catalyst in flowing water vapor, and/or hydroxyl groups on the catalyst. The hydrogen output decreased as shown in Fig. 4a. On the other hand, with increasing pulses of carbon monoxide on pretreated catalyst, the amount of hydrogen decreased as shown in Fig. 4b, which is related to the decrease of chemisorbed hydroxyl groups. IR spectra in Fig. 8 showed that carbon monoxide can react with hydroxyl groups to form adsorbed formate species that decomposed to produce carbon dioxide and hydrogen at the same temperature.

The temperature-programmed surface reaction results, as shown in Fig. 5, showed that the catalyzed reaction on reduced Fe–Ce–Cr–O starts from 473 K in H_2/CO (1:1) mixture.

3.4. In situ FT-IR

For determining the effects of water vapor on Fe–Ce–Cr–O catalyst, adsorbed states of water vapor had been investi-

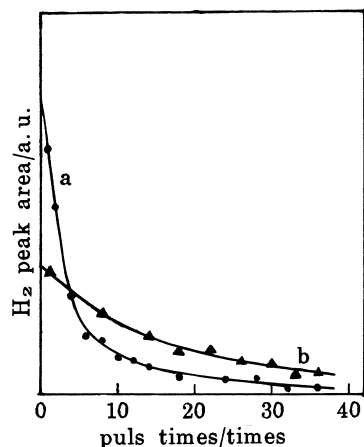


Fig. 4. H_2 output responding the pulse times of H_2O and CO . (a) H_2O and (b) CO .

gated at different temperatures. After an outgassing pretreatment at 653 K, the catalyst was cooled down to room temperature, then contacted with about 1 Torr of water vapor. IR spectra acquired after heating at progressively high temperature are reported in Fig. 6. At temperatures below 473 K, bands at 1634/cm (broad) can be seen. This was attributed to physically adsorbed water. When heating to 573 K, the band disappeared, indicating that weakly adsorbed water desorbed from the surface of Fe–Ce–Cr–O. Two bands at 1357 and 1309/cm, should be paid more attention. We suggest that these two negative peaks are associated with the structure of the catalyst under different temperatures [19,20]. The decrease in intensity of the 1309/cm band with raising the temperature illustrated that the structure represented by 1309/cm was not stable. On the contrary, the intensity of the 1357/cm band underwent a considerable change. It peaked at 473 K, then went down with temperature. These changes showed that the structure represented by the 1357/cm band is stable at high temperatures. The pure Fe_2O_3 exhibited similar intensity changes

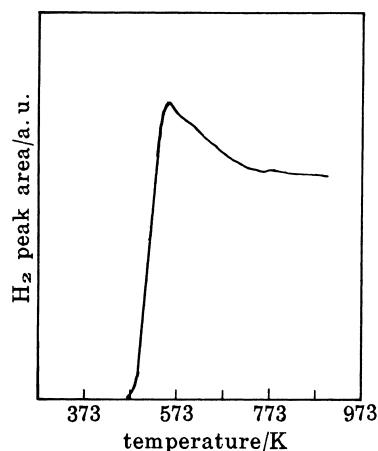


Fig. 5. Temperature-programmed surface reaction on reduced Fe–Cr–Cr–O in H_2O/CO (1:1) mixture.

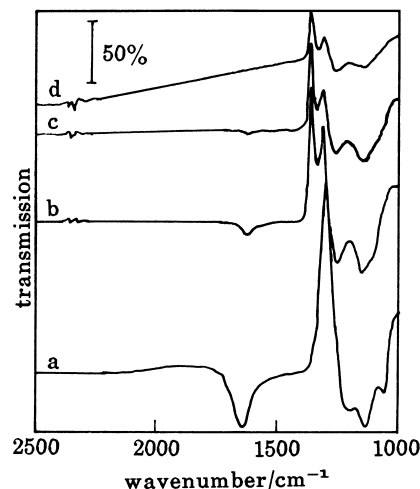


Fig. 6. In situ FT-IR spectra of Fe–Ce–Cr–O in water vapor. (a) room temperature; (b) 473 K; (c) 573 K and (d) 653 K.

in water vapor at moderate temperatures, but the difference was that the 1309/cm band is stable at high temperatures.

Before investigation of the adsorption behavior of the Fe–Ce–Cr–O in CO_2 , the reduced catalyst was heated to 653 K, outgassed, then cooled down to room temperatures and contacted with about 1 Torr of carbon dioxide. The IR spectra were recorded at different temperatures as shown Fig. 7. The bands at 1618, 1411, 1220, 1133/cm were attributed to bicarbonate species by Guenin [13], but the chemisorbed species are not stable at high temperatures. All bands above disappeared at 373 K, however, two strong negative peaks at 1344 and 1305/cm appeared at the same intensity, simultaneously. With raising of the temperatures, the intensity of the 1344/cm band increased, but the intensity of 1305/cm weakened and disappeared at 573 K. We suggest that the two bands at 1305 and 1344/cm could be related to the structure of the catalyst. It is similar with the

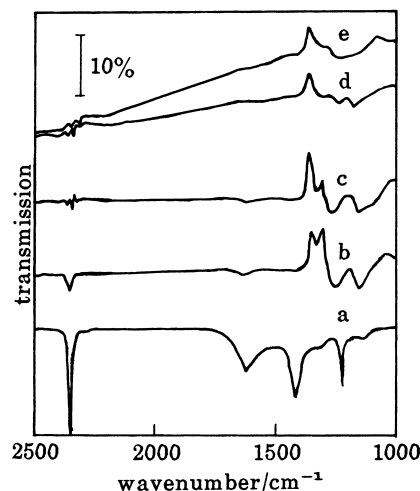


Fig. 7. In situ FT-IR spectra of Fe–Ce–Cr–O in carbon dioxide. (a) room temperature; (b) 373 K; (c) 473 K; (d) 573 K and (e) 653 K.

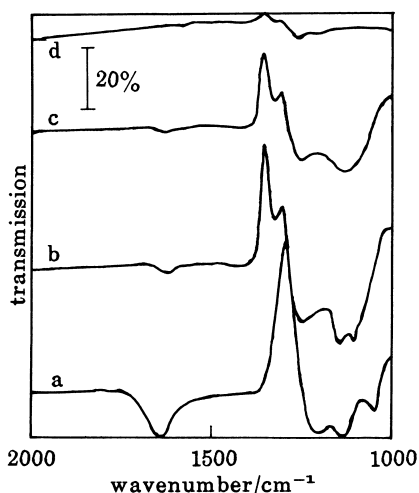


Fig. 8. In situ FT-IR spectra of Fe–Ce–Cr–O in H₂O/CO (1:1) mixture. (a) 373 K; (b) 473 K; (c) 573 K and (d) 653 K.

structure as described above. Most of the carbonate-like species desorbed from the surface of the catalyst at higher temperatures, especially in the reaction temperature range. This is very important for WGSR. The pure Fe₂O₃ is different from Fe–Ce–Cr–O, since the adsorbed carbonate species on the surface still exist at 373 K as shown by TPD in Fig. 2b.

The adsorption behavior of Fe–Ce–Cr–O contacted with 1 Torr H₂O/CO (1:1) mixture is shown in Fig. 8. The shapes of spectra are similar to those of Fig. 6. These IR spectra showed that the reduced surface of the catalyst can only interact with the water vapor in the gas mixture. No carbonate-like species were found on the surface under reaction conditions.

In addition, IR results showed that there are strong broad bands from 2700 to 3700/cm at different temperatures in the presence of water. These bands can be assigned to surface hydroxyl groups.

4. Discussion

4.1. Reduction properties

Comparing the Fe–Ce–Cr–O, Fe–Cr–O and Fe₂O₃ catalysts, the Fe–Ce–Cr–O catalyst has the largest specific surface area and lowest reduction temperature, as shown in Fig. 1. CeO₂ can store and release oxygen, form surface and bulk vacancies, so it can be oxidized by water or carbon oxide. When oxidized by water, it can decompose water producing hydrogen [16]. Pure ceria reacting with carbon dioxide can produce a large amount of stable adsorbed carbonate-like species under WGSR conditions. These species occupied the surface active sites of the catalyst, preventing further reaction. So ceria cannot be used as an effective catalyst for the WGSR [20]. In Fe–Ce–Cr–O,

ceria could form partially intermetallic M–Ce compounds [1], on which carbonate-type species easily decompose under reaction conditions, so we do not observe carbonate species in Figs. 2 and 7 [12]. Here it is ceria which improves the desorption property of the catalyst.

Because the iron-based WGSR catalyst must be reduced to Fe₃O₄ before being used in industry, it is very important to know how to generate a consistent, active and selective reduced catalyst. The TPR results showed that the reduction can be separated into three processes, as the temperature is raised. First, weakly adsorbed oxygen species react with hydrogen in the gas phase at temperatures around 473 K. Second, reaction occurs between lattice oxygen and hydrogen in the temperature range from 423 to 723 K. The largest peak of the profile in Fig. 1 could be included in this process. Third, the Fe₃O₄ phase is further reduced to Fe that is not desired [14,15] at higher temperature than 723 K. The XRD results in previous work [14] show that the main reduction products of three catalysts in the second step are Fe₃O₄. According to the analysis above, we suggest that the optimum reduction temperature range of Fe–Ce–Cr–O should be 423–723 K. In fact, the reduction program of Fe–Ce–Cr–O in industry is separated into four stages (room temperature: 393, 393–543, 543–623, and 623–723 K). The heating rates are 25, 25, 10, and 10 K/h, respectively. The whole reduction time is about 60 h.

4.2. Reaction properties

On the surface of reduced Fe–Ce–Cr–O there is a large amount of adsorbed material. This, especially the water, must be removed in an IR cell under vacuum at 773 K until the IR spectrum of the sample is stable. In general, the clean surface of a reduced catalyst has a large number of anion vacancies [16–18]. After water vapor was introduced into the IR cell, IR spectra were recorded at different temperatures. As can be seen in Fig. 6, at low temperatures the spectra mainly related to weakly absorbed water. Water, as reported by Otsuka et al. [16], could oxidize the reduced metallic oxide as oxidizer. They found some intermediate oxides and that the metal ions occupy crystallographically equivalent positions regardless of charge, and that there is a very small cation shift in position from one structure to another. When the reduced CeO₂ was oxidized by oxygen or other oxidizers, Li et al. [19,20] found negative bands near 1340 and 1000/cm, and pointed out that this was caused by the oxygen vacancies formed by reduction being filled with the oxygen ions of the oxidizers. These results are consistent with our work.

Water vapor and carbon dioxide are stronger oxidizers than the reduced metal oxides, but water vapor is a stronger oxidizer than carbon dioxide to the reduced Fe–Ce–Cr–O catalyst as shown by IR spectra in Figs. 6 and 7. In the WGSR gaseous mixture, water vapor played an important role in the oxidization of catalyst under reaction conditions. This suggests that water can interact with surface vacancies

and decompose to form H or adsorbed hydroxyl groups. TPD investigations of water vapor and carbon dioxide are consistent with this viewpoint. The total quantity of adsorbed carbon dioxide was obviously lower than that of water under the same conditions. The desorption temperature of adsorbed carbon dioxide and carbonate-like species, as shown in Fig. 2, was lower than water.

When raising the adsorption temperatures, the two IR spectra intensities at 1309 and 1344/cm for water decrease. But the behavior of the two peaks are very different. The intensities of the two peaks can be used to indicate the stability of the surface states. These suggest that the carbonate-like species produced by the WGSR is more easily desorbed from the surface of the catalyst.

Either in water vapor or carbon dioxide, the surface states represented by 1309/cm are only stable at low temperatures; but the state represented by 1344/cm is stable, as shown in Figs. 6 and 7. Under reaction temperatures (from 573 to 673 K), the main state of the catalyst can be represented by 1344/cm, and the IR spectra in H₂O/CO mixture showed similar results. The weakly adsorbed water and carbon dioxide represented by 1634 and 2465/cm, respectively, are absent at the same temperatures.

The pulse reaction results showed that the reduced Fe–Ce–Cr–O decomposes water, and produces hydrogen at moderate temperature. The most important equipment for the reaction is that the catalyst must be in a reduced state. The results in Fig. 4 indicate that the hydrogen output decreases with the pulse times. We supposed that the oxygen vacancies on the reduced surface are limited. After reacting with water, they decreased rapidly until they completely vanished. Obviously, it is very important that the surface re-oxidized by water must be reduced again to provide enough effective surface. Carbon monoxide can be used to do this.

4.3. Reaction mechanism

According to the investigation described above, a redox mechanism is suggested to explain the WGSR on the Fe–Ce–Cr–O catalyst at reaction temperatures. It can be described by a two-step cycle: first step, water oxidizes the reduced catalyst forming hydrogen and adsorbed hydroxyl groups (Figs. 3 and 4). In this step, the reduced surface containing anion vacancies splits the HO–H bond, two neighboring activated H combine to form hydrogen; the hydroxyl group is adsorbed on the catalyst surface. In reductive gases, this hydroxyl group is difficult to decompose by itself or desorb from the surface (Figs. 3, 4 and 8). Second step, carbon monoxide interacts with hydroxyl groups forming formate-like species, then formate species react with water or hydroxyl groups to produce carbon dioxide and hydrogen. At the same time, the catalyst recovers. Shido [21] suggested that water can prevent the backward

decomposition of formates to CO and OH groups. Hydrogen can be generated in both steps, but the reaction rate is too fast to investigate the detailed intermediates at reaction temperatures by IR spectroscopy.

5. Conclusions

The TPR profiles of three catalysts suggest that the reducibility of Fe–Ce–Cr–O is the best, and its optimum reduction temperature range is 423–723 K.

The reduced Fe–Ce–Cr–O can be oxidized by water and carbon dioxide at reaction temperatures (from 573 to 673 K), but no carbonate-like adsorbed species were found on the catalyst by IR spectroscopy at these temperatures.

Water can be decomposed to form hydrogen on the reduced catalyst, and carbon monoxide can react with hydroxyl groups on the catalyst to produce hydrogen and carbon dioxide, simultaneously.

A redox mechanism can be used to explain the WGSR occurring on Fe–Ce–Cr–O.

Acknowledgements

This work has been supported by National Nature Science Foundation of China.

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