Improving Catalytic Performance of Ethane Dehydrogenation in the Presence of CO₂ over Zr-Promoted Cr/SiO₂

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ABSTRACT: The Zr-, Ce-, Sr-, and Sn-promoted Cr/SiO₂ catalysts were prepared by the incipient wetness impregnation method, then characterized by N₂ adsorption/desorption, X-ray diffraction, X-ray photoelectron spectroscopy, H₂-TPR, CO₂-TPD, UV-Vis, high-angle annular dark-field imaging—scanning transmission electron microscopy—energy dispersive X-ray spectroscopy—elemental mapping, Raman, and thermogravimetric techniques to study the structural evolution under the preparation/reaction conditions, and applied to catalyze ethane oxidative dehydrogenation with CO₂. The results suggested that the Cr⁶⁺ species were indispensable for activating the dehydrogenation reaction thanks to the oxidation—reduction cycle between Cr⁶⁺ and Cr⁴⁺. The type of the promoter also affected significantly the ability of replenishing the lattice oxygen through the dissociation of CO₂, leading to the different catalytic performances. The Zr-promoted sample had the best performance in converting the reactants as well as the catalytic stability.

1. INTRODUCTION

With the increase of population in the world, the consumption of fossil-based resources increases sharply. The emission of CO₂ is accumulated in the atmosphere, and further enhances the “greenhouse effect”. Therefore, a large number of endeavors are paid to technologies including carbon dioxide capture, utilization, and storage. On the other hand, the large-scale exploitation of shale gas, together with the other unconventional natural gas sources, offers abundant but cheap light alkanes mainly methane and ethane. Dry reforming of methane is widely studied in recent years as it could convert the two major greenhouse gases simultaneously into syngas. Ethylene as a chemical building block could be subsequently applied to the Fischer–Tropsch synthesis as raw materials. In the case of ethane, it supplies which could be subsequently applied to the Fischer–Tropsch synthesis as raw materials. In the case of ethane, it supplies.

CO₂ takes place easily compared to the noncatalytic thermal dehydrogenation process (eqs 1 and 2). In addition, it is helpful to remove the deposited coke through reacting with CO₂:

\[
\begin{align*}
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 & \Delta H_{298 K}^0 &= 137 \text{ kJ/mol} \quad (1) \\
\text{C}_2\text{H}_4 + \text{CO}_2 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{CO} & \Delta H_{298 K}^0 &= 134 \text{ kJ/mol} \quad (2)
\end{align*}
\]

Cr-based catalysts are widely applied to catalyze oxidative dehydrogenation of ethane with CO₂ because the Cr element has a multioxidative state, which is favorable to form the oxidation—reduction cycle between the high and low chemical valents. Deng et al. synthesized the Cr/ZrO₂ catalysts and introduced Ni, Fe, Co, and Mn as promoters. It was found that the addition of Fe, Co, and Mn could enhance the selectivity of ethylene, while the sample modified by Ni promoted the side reaction like the reforming reaction; as a result, CO was preferred to generate. Such a product distribution was probably related to the strong ability of Ni in cleaving C–C and C–H bonds. Similar results could be also observed in the other Ni-contained catalysts such as PtNi and FeNi systems. The silica-based materials are most commonly used as supports. The experimental results from Wang and Baiker further confirmed that the support SiO₂ performed better than Al₂O₃, ZrO₂, TiO₂, and even their composites with SiO₂. The reported silica-based material-supported Cr catalysts included Cr/MCM-41, Cr/MSU-x, Cr/ZSM-S₅, Cr/Zr-ZSM-S₅, and Cr/SAPO-
34,26 Obviously, the research on the support effect is very active for the Cr family catalysts, and the silica-based materials attract most attention just because the appropriate properties of the catalyst such as the dispersion of Cr species, redox and acid–base which are favorable for ethane dehydrogenation with CO2 could be obtained. However, the publications on the promoter effect of Cr-based catalysts are limited.

Therefore, the present work would focus on the promoter effect of the Cr-based catalyst where a commercial SiO2 is chosen as the support, and the metal elements including Zr, Ce, Sr, and Sn would be introduced into the base sample Cr/SiO2 as promoters because: (i) the introduction of ZrO2 can improve the acid–base and redox properties, generate abundant oxygen vacancies,14,15,27 (ii) CeO2 shows very strong capacity in oxygen storage, release, and transport,28–30 (iii) Sr could be incorporated into the catalyst matrix and thus modify the acid–base property. The deep oxidation of ethane is expected to be limited,31,32 (iv) the existence of Sn can restrict the side reactions, and improve the coke resistance.32–34 This series of promoted catalysts is prepared by the conventional incipient wetness impregnation (ICI) method, and characterized by various techniques to obtain the physicochemical properties which are further correlated with catalytic performances in dehydrogenation of ethane in the presence of CO2.

2. RESULTS AND DISCUSSION

2.1. Porosity.

The textural properties including the specific surface area, pore volume, and average pore diameter were measured by N2 adsorption/desorption isotherms which were depicted in Figure 1(l). All the samples showing the similar adsorption/desorption behaviors as the type IV isotherms were obtained according to the IUPAC classification,33 which was the characteristic of mesoporous materials. The capillary condensation occurred between 0.65 and 0.95 of relative pressure, and therefore gave the type H2 hysteresis loop which was directly linked to the uniformity of the pores. The pore size distribution also showed similar results (centered at around 12 nm) as seen from Figure 1(r), suggesting that the microstructure was similarly affected after loading 12 wt % metals on the support.

More precise information could be obtained from the quantified results that were listed in Table 1. Comparing with the pristine SiO2 support, the surface areas of supported catalysts decreased by from 25.8% for CeCr/SiO2 to 33.7% for ZrCr/SiO2, both the values were much bigger than the metal loading of 12 wt %, indicating that pores were partially plugged by the metal species, which could be further evidenced by the loss of the pore volume. On the other hand, the average diameters of Zr-, Sr-, and Sn-promoted samples were identical to ~12.7 nm which was even bigger than that of the support. Such a result was probably caused by plugging the pore with a smaller diameter because a wide distribution between 3 and 30 nm could be found for the support. The smaller average diameters of CeCr/SiO2 and Cr/SiO2 (~9.9 nm for the both) may imply better dispersion of metal species on the support.

2.2. Crystalline Phase. The X-ray diffraction (XRD) results of the calcined samples are reported in Figure 2(l), the broad diffraction peak at ~22° was assigned to the amorphous SiO2 support. The evident diffractions from Cr2O3 could be found at 24.6, 33.6, 36.3, 41.5, 50.3, 54.9, 63.5, 65.2, and 73.1° for all the samples. It was interesting to note that the diffractions from the second metal species were hard to detect, which may be caused by their quite low content and/or by well-dispersed nanoparticles. The XRD patterns for the spent catalysts are depicted in Figure 2(r), and no obvious change was found except for the ZrCr/SiO2 sample over which the quartz phase was detected, which was probably caused by the residual quartz sand.

2.3. Surface Analysis. The chemical state of surface elements was measured on both calcined and spent catalysts by the X-ray photoelectron spectroscopy (XPS) technique to explore the possible evolution during the reaction, the Cr 2p3/2 XPS spectra are reported in Figure 3. Two isolated peaks were observed, corresponding to the Cr species centered at ~576.5 eV and its satellite peak which usually appeared at the 9.3 eV higher binding energy side, centered at ~585.8 eV. The Cr species involved at least two types of chemical states according to the deconvolution treatment, the peaks at a binding energy
of ∼576 and ∼580 eV were assigned to Cr$^{3+}$ and Cr$^{6+}$, respectively. Besides these, another peak appeared at the lower binding energy side (∼573 eV) for all the samples except ZrCr/SiO$_2$, but its origin was really unclear, and the unknown Cr species were denoted as Cr$^x$.

According to the quantification of surface composition that was listed in Table 2, it could be found that the surface content of Cr was different, and showed a decreasing order as: SnCr/SiO$_2$ (1.3%) > Cr/SiO$_2$ (1.1%) > CeCr/SiO$_2$ (1.0%) > ZrCr/SiO$_2$ (0.7%) > SrCr/SiO$_2$ (0.6%). While for the promotor, the surface contents of Zr and Ce had the same values as that of the surface Cr in corresponding samples, the surface content of Sn was about one-fourth time as high as that of surface Cr. It was interesting to note that no Sr was detected on the catalyst surface by XPS. As far as the chemical state of the Cr species was concerned, the sample ZrCr/SiO$_2$ showed the maximum proportion of Cr$^{6+}$ (64.0%), and SrCr/SiO$_2$ showed the minimum value of 1.3%. Compared to the unpromoted Cr/SiO$_2$, the content of Cr$^{6+}$ species was higher for Zr- and Sn-promoted catalysts, meaning that the Cr$^{6+}$ species were easier
to form during the calcination process. On the contrary, the addition of Sr and Ce could stabilize the Cr$^{3+}$ species.

The Cr 2p$_{3/2}$ spectra had obvious changes, the Cr$^{3+}$ species became the majority in each sample because of the reduction by alkane during the reaction. Only quite small peaks assigned to Cr$^{6+}$ species could be seen for Cr/SiO$_2$ and CeCr/SiO$_2$, and it disappeared completely for SrCr/SiO$_2$ and SnCr/SiO$_2$ samples, and a new shoulder at around 582 eV appeared instead, which could be also found for CeCr/SiO$_2$. The quantified results in Table 3 exhibited that all Cr species existed as Cr$^{3+}$ (100%) in catalysts SrCr/SiO$_2$ and SnCr/SiO$_2$. The Cr$^{6+}$ species took up only 2.9 and 0.09% in CeCr/SiO$_2$ and Cr/SiO$_2$, respectively. The Zh-promoted ZhCr/SiO$_2$ catalyst still involved the maximum of Cr$^{6+}$ after the catalytic reaction, although a part of them was converted into the ill-defined Cr$^x$ species. Another evident change was from the surface composition, the increase of the Cr surface content indicated that the Cr species was enriched under the reaction conditions, while the surface content of the promotors did not show any specific trend. The Sr species that were found on the surface of the calcined sample were detected in the spent one. These results suggested that a dynamic surface existed during the reaction which may be driven by the redox process.

The O 1s spectra for the catalysts before reaction (BR) are shown in Figure 4, and it involved three types of oxygen species for all the samples as three peaks could be obtained through deconvolution treatment. The one at a lower binding energy of 531.5 eV was from the surface lattice oxygen (O$_1$), the one at a binding energy of ~532.3 eV was attributed to hydroxyl oxygen (O$_{II}$), while the one at a higher binding energy of ~533.6 eV was assigned to the adsorbed water species (O$_{III}$). It has been reported that hydrogen could react with lattice oxygen to generate M$^{-}$OH and oxygen vacancies. Moreover, the charge balance was kept by bonding the metal cations with OH groups. Obviously, the number of surface hydroxyl oxygen (O$_{II}$) could reflect directly the quantity of oxygen vacancies. The quantitative results in Table 4 show that the percentage of surface hydroxyl oxygen followed the decreasing trend like: ZrCr/SiO$_2$ (47.5%) > CeCr/SiO$_2$ (42.9%) > SnCr/SiO$_2$ (38.3%) > Cr/SiO$_2$ (34.1%) > SrCr/SiO$_2$ (33.9%). It suggested that a larger number of oxygen vacancies could be created when Cr was partially substituted by Sn, Ce, and Zr.

The three types of oxygen still coexisted from the O 1s spectra for the catalysts after reaction (AR), while their proportions changed according to the results in Table 5. The percentage of surface lattice oxygen decreased by different

| catalyst        | Cr$^{6+}$ | Cr$^{3+}$ | Cr$^x$ | M/Cr/Si/O | Cr$^{6+}$/Cr$^{3+}$/Cr$^x$ |
|-----------------|-----------|-----------|--------|-----------|---------------------------|
| ZrCr/SiO$_2$    | 579.8     | 576.8     | 574.2  | 0.3/1.0/24.2/74.5 | 27.8/59.7/12.5          |
| SrCr/SiO$_2$    |           |           |        | 0.2/1.5/21.5/76.8 | 0/100/0                  |
| SnCr/SiO$_2$    |           |           |        | 0.4/2.1/20.9/76.6 | 0/100/0                  |
| CeCr/SiO$_2$    | 580.6     | 576.4     | 573.1  | 0.5/1.1/22.4/76.0 | 2.9/72.0/25.1           |
| Cr/SiO$_2$      | 580.4     | 575.6     |        | —/1.3/20.5/78.2  | 0.09/99.1/0              |

Figure 4. O 1s XPS spectra for different samples BR and AR (a) ZrCr/SiO$_2$, (b) SrCr/SiO$_2$, (c) SnCr/SiO$_2$, (d) CeCr/SiO$_2$, and (e) Cr/SiO$_2$. The O 1s spectra for the catalysts before reaction (BR) are shown in Figure 4, and it involved three types of oxygen species for all the samples as three peaks could be obtained through deconvolution treatment. The one at a lower binding energy of 531.5 eV was from the surface lattice oxygen (O$_1$), the one at a binding energy of ~532.3 eV was attributed to hydroxyl oxygen (O$_{II}$), while the one at a higher binding energy of ~533.6 eV was assigned to the adsorbed water species (O$_{III}$). It has been reported that hydrogen could react with lattice oxygen to generate M$^{-}$OH and oxygen vacancies. Moreover, the charge balance was kept by bonding the metal cations with OH groups. Obviously, the number of surface hydroxyl oxygen (O$_{II}$) could reflect directly the quantity of oxygen vacancies. The quantitative results in Table 4 show that the percentage of surface hydroxyl oxygen followed the decreasing trend like: ZrCr/SiO$_2$ (47.5%) > CeCr/SiO$_2$ (42.9%) > SnCr/SiO$_2$ (38.3%) > Cr/SiO$_2$ (34.1%) > SrCr/SiO$_2$ (33.9%). It suggested that a larger number of oxygen vacancies could be created when Cr was partially substituted by Sn, Ce, and Zr. The three types of oxygen still coexisted from the O 1s spectra for the catalysts after reaction (AR), while their proportions changed according to the results in Table 5. The percentage of surface lattice oxygen decreased by different
existence of Cr$_3^+$ species in Cr$_2$O$_3$ or CrO
While the presence of bands at 460 and 600 nm con-
transition of chromate species in tetrahedral coordination.

vis spectroscopy, and the collected spectra were depicted in

The redox ability of the Cr species was measured by H$_2$-TPR, and the profiles are shown in Figure 7. It was obvious that the continuous hydrogen consumption took place between 250 and 600 °C for each catalyst, corresponding to the reduction of Cr$_{\text{VI}}$ to Cr$_{\text{III}}$. The broad and overlapped reduction peaks may suggest one or more transition states, for example, Cr$_{\text{III}}$ existed in the reduction process. The hydrogen consumption could be roughly divided into three stages: (i) the low temperature range between 250 and 350 °C, corresponding to the reduction of Cr$_{\text{VI}}$ species located in the vacancy defect sites or in the corner, edge, and vertex of the lattice; (ii) the medium temperature range between 350 and 440 °C,
corresponding to the Cr$^{6+}$ species on the lattice surface; and (iii) the high temperature range from 440 to 600 °C, corresponding to the reduction of bulk Cr$^{6+}$ species.

Although the reduction of each catalyst took place in the same temperature zone, the reduction behaviors were dependent on the type of the promoter. The quantity of consumed hydrogen listed in Table 6 shows that the ZrCr/SiO$_2$ sample had a maximum value of 1.36 mmol/gcat., which was a little bit more than that for the SrCr/SiO$_2$ sample (1.35 mmol/gcat.). The promotor-free sample Cr/SiO$_2$ had the least hydrogen consumption (0.75 mmol/g cat.). Moreover, the hydrogen consumption distribution was also different. ZrCr/SiO$_2$ and CeCr/SiO$_2$ exhibited the main hydrogen consumption in a low temperature range, SrCr/SiO$_2$ and Cr/SiO$_2$ showed larger hydrogen consumption in a high temperature range, while the sample SnCr/SiO$_2$ had the similar values in low and high temperature ranges. The results demonstrated that the introduction of promotors could efficiently enhance the reduction of Cr$^{6+}$ species, but it also made the reduction of bulk Cr$^{6+}$ species more difficult as a higher temperature was needed. The addition of Zr and Ce improved significantly the reduction of Cr$^{6+}$ species on the lattice surface.

2.7. Basicity by CO$_2$-TPD. The basicity of catalysts was analyzed by the temperature-programmed desorption (TPD) method using CO$_2$ as a probing molecule, and the desorption profiles are recorded as shown in Figure 8. Similar CO$_2$ desorption behaviors could be found for all the samples, showing two desorption zones, the one below 400 °C represented the CO$_2$ desorbed from weak basic sites, while the other one occurring at a higher temperature could be considered as the desorption of CO$_2$ from strong basic ones. The desorption behaviors did not change significantly, which was probably related to the low loading of promotors. On the other hand, the introduction of promotors had a profound effect the number of basic sites. According to the quantification results shown in Table 6, CO$_2$ uptake increased by 18.4% to 1.14 mmol/gcat. for sample ZrCr/SiO$_2$ compared with that for

Table 6. Quantifications for H$_2$-TPR, CO$_2$-TPD, TG, and Raman Analysis

| catalyst   | H$_2$ consumption, mmol/gcat. | CO$_2$ uptake, mmol/gcat. | coke, mgC/gcat. | I$_D$/I$_G$ |
|------------|-------------------------------|--------------------------|-----------------|------------|
| ZrCr/SiO$_2$ | 1.36                          | 1.14                      | 38.8            | 1.22       |
| SrCr/SiO$_2$ | 1.35                          | 0.89                      | 22.2            | 1.18       |
| SnCr/SiO$_2$ | 1.03                          | 0.73                      | 15.9            | 1.45       |
| CeCr/SiO$_2$ | 0.93                          | 0.94                      | 40.6            | 1.28       |
| Cr/SiO$_2$  | 0.75                          | 0.93                      | 67.9            | 1.35       |

Figure 6. Raman spectra for (l) calcined and (r) spent catalysts (a) ZrCr/SiO$_2$, (b) SrCr/SiO$_2$, (c) SnCr/SiO$_2$, (d) CeCr/SiO$_2$, and (e) Cr/SiO$_2$.

Figure 7. TPR profiles for different catalysts (a) ZrCr/SiO$_2$, (b) SrCr/SiO$_2$, (c) SnCr/SiO$_2$, (d) CeCr/SiO$_2$, and (e) Cr/SiO$_2$.

Figure 8. CO$_2$-TPD profiles for different samples (a) ZrCr/SiO$_2$, (b) SrCr/SiO$_2$, (c) SnCr/SiO$_2$, (d) CeCr/SiO$_2$, and (e) Cr/SiO$_2$.
the promotor-free Cr/SiO₂ sample (0.93 mmol/gcat). The introduction of Ce had increased it slightly to 0.94 mmol/gcat, while the addition of Sr and Sn played negative effects on the number of basic sites, resulting in 0.89 mmol/gcat for SrCr/SiO₂ and 0.73 mmol/gcat for SnCr/SiO₂. It was clear that the introduction of Zr was favored to enhance the adsorption of CO₂ on the catalyst surface, which would be further activated and afterward compensate the consumed lattice oxygen by linking it with the XPS findings.

2.8. Coke Deposition by TG. The coke deposition took place under the reaction conditions, which has been proved by the Raman measurements, and the disordered carbon was the majority. The quantification of coke was proceeded by running the thermogravimetric (TG) test in diluted oxygen on the spent catalysts, and the TG curves are presented in Figure 9.

![Figure 9. TG analysis for the spent catalysts (a) ZrCr/SiO₂, (b) SrCr/SiO₂, (c) SnCr/SiO₂, (d) CeCr/SiO₂, and (e) Cr/SiO₂.](image)

showing a continuous weight loss process for all the samples. The main weight loss due to the combustion of coke occurred between 450 and 600 °C, and no isolated peak could be found from derivative TG curves for the SrCr/SiO₂ and SnCr/SiO₂ samples, meaning that the quantity of coke was rather small. The calculated quantity of coke in Table 6 shows that the additives could efficiently suppress the coke formation during the reaction compared with that for the Cr/SiO₂ catalyst (67.9 mgC/gcat). SrCr/SiO₂ and SnCr/SiO₂ showed less quantity of coke among the promoted catalysts as only 22.2 and 15.9 mgC/gcat. was formed, respectively. On the other hand, the bigger pore diameter may play a positive role in restricting the coke deposition, just because the larger space offered enough carbon capacity and promoted the coke elimination reaction (CO₂ + C → 2CO).

2.9. Morphology. The dispersion of different elements was checked by performing the high-angle annular dark-field imaging (HAADF)—scanning transmission electron microscopy (STEM) integrated with energy dispersive X-ray spectroscopy (EDS) element mapping measurements, and the images are depicted in Figure 10. It could be seen that the Cr species were well dispersed in the calcined catalysts (a,c), and no evident aggregation was found from the spent ones (b,d). The carbonaceous substance was detected for both the spent catalysts, indicating the occurrence of coke deposition during the reaction.

2.10. Catalytic Dehydrogenation of Ethane with CO₂. The various metal-promoted Cr/SiO₂ catalysts were applied to catalyze ethane dehydrogenation with CO₂, and the reaction data are listed in Table 7. Compared with the promotor-free sample Cr/SiO₂, the Zr- and Ce-promoted catalysts showed the increasing of ethane conversion (38.3% for ZrCr/SiO₂ and 32.3% for CeCr/SiO₂), whereas the introduction of Sr and Sn had negative influences on it, leading to a decrease in ethane conversion to 26.6 and 25.0% for SrCr/SiO₂ and SnCr/SiO₂ catalysts, respectively. As far as the product distribution was concerned, the desired product ethylene together with CO was the major parts for all the catalysts. Methane was also found in the product, but the proportion of it was quite small (<2.0%).

The calculation of turnover frequency (TOF) allowed us to understand deeply the influence of the promotor on Cr species and further on catalytic conversion of ethane in the presence of CO₂. The TOF values calculated on the basis of total Cr is shown in Table 7, exhibiting a medium value of 0.20 s⁻¹ for the Cr/SiO₂ sample. It increased by 20% to 0.24 s⁻¹ when Cr was partially substituted by Ce, and reached the maximum of 0.32 s⁻¹ for ZrCr/SiO₂, which was at least 2 times as high as those for SrCr/SiO₂ (0.16 s⁻¹) and SnCr/SiO₂ (0.15 s⁻¹). These results indicated that the addition of Ce and Zr was favored to form more active Cr species to improve the catalytic activity, while the Sn and Sr additives acted in opposite roles.

The long-term stability was investigated by running the 100 h time on stream catalytic reactions, the performances including the initial conversions (X₀), final conversions (Xₙ) of reactants, and the selectivity of the desired product ethylene (Sₐ,C,H₄) are shown in Table 8 and the tracks of them are shown in Figure 11. The initial conversions of ethane on ZrCr/SiO₂ and CeCr/SiO₂ were 57.1 and 52.6%, respectively, both of which were higher than that on Cr/SiO₂ (48.5%), confirming again the promotion of Zr and Ce in activation of ethane. As abovementioned, the Sr and Sn additives could limit the conversion activation of ethane, and the ethane conversion consequently dropped down. All the catalysts showed a similar selectivity of ethylene with the exception of Sn, like the 8 h time on stream reaction results presented in Table 7, suggesting that ethylene was more selective on the SnCr/SiO₂ sample. The catalysts showed a similar ability to activate the oxidant CO₂.

Concerning the stability, SrCr/SiO₂ and SnCr/SiO₂ deactivated in the first 10 h and then remained nearly unchanged, and the conversion of ethane lost around 26.8 and 6.4%, respectively. Over the sample ZrCr/SiO₂, the conversion of ethane decreased sharply by ~37% from 57.1 to 36.0% in the first 20 h, and then continued decreasing gently to 32.1% at the end of the reaction. The analogue experiences could be also found over CeCr/SiO₂ and Cr/SiO₂, and it lost more than 40% in the test range. It took less time to get the steady state for conversion of CO₂ compared with that of ethane although fast deactivation was observed as well. SrCr/SiO₂ and SnCr/SiO₂ reached the steady state after reacting for 10 h which was prolonged to 20 h for the rest. Ethylene selectivity climbed up in the first 10 h for all the samples and then kept nearly constant.

2.11. Discussion. The introduction of the promotors like Ce, Zr, Sr, and Sn into the Cr/SiO₂ system had significant influences on the catalyst microstructure and surface property, which further determined the catalytic performance and catalytic stability. The key properties of catalysts including the proportion of Cr⁶⁺ species, lattice oxygen (O₁) and hydroxyl oxygen (O₂), and the initial activity are correlated in Figure 12. The samples SrCr/SiO₂ and SnCr/SiO₂ showed
even lower initial conversions of both ethane and CO$_2$ reactants, the Cr$^{6+}$ species were absent although they could be found in the calcined catalysts, meaning that the Cr$^{6+}$ species underwent the irreversible reduction to lower and less active Cr$^{3+}$ species. On the other hand, both lattice oxygen (O$_I$) and hydroxyl oxygen (O$_{II}$) increased for CeCr/SiO$_2$ and ZrCr/SiO$_2$ samples compared with the pristine Cr/SiO$_2$.

During the reaction, the ethane molecule was adsorbed on Cr$^{6+}$ species and oxidized by lattice oxygen, leaving the oxygen vacancy defect and generating hydroxyl oxygen (O$_{II}$) simultaneously. Therefore, higher catalytic activity was obtained over the CeCr/SiO$_2$ and ZrCr/SiO$_2$ samples which involved more active Cr$^{6+}$ species and lattice oxygen (O$_I$). The reduced Cr$^{3+}$ species was reoxidized to Cr$^{6+}$ species by CO$_2$ and the oxygen vacancy was thus refilled. As a consequence, the CO$_2$ conversion increased with the increasing of hydroxyl oxygen (O$_{II}$) which was directly linked to the oxygen vacancy as mentioned in the XPS part. This result was in good agreement to the experimental data. Obviously, the Cr$^{6+}$ species were indispensable to improve the catalytic activity, and it ensured that the redox cycle of Cr species works smoothly. The type and number of oxygen species were related to the redox and ability of CO$_2$ activation, resulting in the difference in conversions of ethane and CO$_2$. Based on these results, a possible reaction route was proposed as shown in Figure 13.

Concerning the catalytic stability for dehydrogenation of ethane in the presence of CO$_2$, all the catalysts showed a fast

Table 7. Catalytic Performance over Various Catalysts$^a$

| catalyst       | TOF, s$^{-1}$ | C$_2$H$_6$ conversion, % | CO$_2$ conversion, % | C$_2$H$_4$ selectivity, % | CH$_4$ selectivity, % | CO selectivity, % |
|----------------|---------------|----------------------------|----------------------|---------------------------|----------------------|------------------|
| ZrCr/SiO$_2$   | 0.32          | 38.3                       | 29.2                 | 72.1                      | 1.3                  | 26.6             |
| SrCr/SiO$_2$   | 0.16          | 26.6                       | 31.8                 | 70.4                      | 0.9                  | 28.8             |
| SnCr/SiO$_2$   | 0.15          | 25.0                       | 21.4                 | 82.1                      | 0.6                  | 17.3             |
| CeCr/SiO$_2$   | 0.24          | 32.3                       | 26.9                 | 69.0                      | 1.0                  | 30.0             |
| Cr/SiO$_2$     | 0.20          | 31.8                       | 26.8                 | 68.8                      | 1.4                  | 29.8             |

$^a$Reaction conditions: mass of the catalyst = 300 mg, atmospheric pressure, temperature = 700 °C, flowrate of reactants = 30 mL·min$^{-1}$, time on stream = 8 h. $^b$The TOF was calculated on the basis of total Cr.

Table 8. Long-Term Catalytic Performance for Various Catalysts

| catalyst       | X$_{0}$ C$_2$H$_6$ | X$_{f}$ C$_2$H$_6$ | $\Delta$C$_{C_2H_6}$ | X$_{0}$ CO$_2$ | X$_{f}$ CO$_2$ | $\Delta$C$_{CO_2}$ | S$_{C_2H_6}$ |
|----------------|---------------------|---------------------|----------------------|---------------|---------------|----------------------|-------------|
| ZrCr/SiO$_2$   | 57.1                | 32.1                | 43.7                 | 45.2          | 26.1          | 42.2                 | 76.1        |
| SrCr/SiO$_2$   | 32.1                | 23.5                | 26.8                 | 26.9          | 21.5          | 20.1                 | 77.2        |
| SnCr/SiO$_2$   | 27.7                | 25.9                | 6.4                  | 25.0          | 22.0          | 12.2                 | 89.2        |
| CeCr/SiO$_2$   | 52.6                | 27.9                | 24.7                 | 43.0          | 24.8          | 42.3                 | 70.3        |
| Cr/SiO$_2$     | 48.5                | 25.4                | 47.6                 | 41.2          | 22.5          | 45.4                 | 73.8        |

During the reaction, the ethane molecule was adsorbed on Cr$^{6+}$ species and oxidized by lattice oxygen, leaving the oxygen vacancy defect and generating hydroxyl oxygen (O$_{II}$) simultaneously. Therefore, higher catalytic activity was obtained over the CeCr/SiO$_2$ and ZrCr/SiO$_2$ samples which involved more active Cr$^{6+}$ species and lattice oxygen (O$_I$). The reduced Cr$^{3+}$ species was reoxidized to Cr$^{6+}$ species by CO$_2$ and the oxygen vacancy was thus refilled. As a consequence, the CO$_2$ conversion increased with the increasing of hydroxyl oxygen (O$_{II}$) which was directly linked to the oxygen vacancy as mentioned in the XPS part. This result was in good agreement to the experimental data. Obviously, the Cr$^{6+}$ species were indispensable to improve the catalytic activity, and it ensured that the redox cycle of Cr species works smoothly. The type and number of oxygen species were related to the redox and ability of CO$_2$ activation, resulting in the difference in conversions of ethane and CO$_2$. Based on these results, a possible reaction route was proposed as shown in Figure 13.

Concerning the catalytic stability for dehydrogenation of ethane in the presence of CO$_2$, all the catalysts showed a fast
deactivation process during the initial stage although different promotors had different effects on the conversions of the reactants. It was mainly caused by the deposited coke because the aggregation of Cr species was not evidently observed from the HAADF−STEM analysis. The quantity of deposited coke determined by TG and the variation in conversions of ethane and CO₂ are plotted in Figure 14. Overall, the conversions of both ethane and CO₂ lost less catalysts with less quantity of coke. The additives Zr and Ce were good to improve the conversion of reactants, meanwhile to enhance the resistance to coke. The Sr- and Sn-promoted samples showed a lower level of coke, the lower reaction extent including coke formation reactions may also contribute to it.

3. CONCLUSIONS

Cr in pristine Cr/SiO₂ was partially substituted by Zr, Sr, Sn, and Ce to give metal-promoted catalysts. Such a modification did not bring considerable changes in porosity. The Cr⁶⁺ species were not detected by XRD because of the good dispersion, whereas they could be found from XPS, UV−vis, and Raman measurements. The surface composition as well as the chemical states of Cr and O were significantly affected, and the Cr⁶⁺ species was irreversibly reduced to Cr³⁺ which was less active for dehydrogenation of ethane with CO₂ when Sr and Sn were introduced, restricting the conversion of ethane. The addition of Zr and Ce enhanced the reduction of Cr⁶⁺ species on the lattice surface according to TPR and generated more active oxygen species including the lattice oxygen and hydroxyl oxygen, which promoted the conversions of ethane with CO₂. The catalytic deactivation was caused by deposited coke regardless of the aggregation of Cr species through combining the morphology, Raman, and TG studies. The TOF
calculation showed that the Zr promoter performed the best among the promoted catalysts, and finally the highest initial conversion ethane (~57%) was obtained. At the same time, it also showed better catalytic stability during 100 h time on the stream reaction among the catalysts with the "promotion effect".

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. The catalysts were prepared by the ICI method. SiO2 was activated at 500 °C for 4 h to remove the adsorbed water and impurities prior to use. The precursor of the promoter (Zr(NO3)4·5H2O, Sr(NO3)2, SnCl2, and Ce(NO3)3·6H2O as Zr, Sr, Sn, and Ce sources, respectively) and Cr source (Cr(NO3)3·9H2O) were dissolved in a certain amount of deionized water to get the impregnation solution. The solids were dried at 70 °C overnight after the ICI process, and then calcined at 600 °C for 4 h in static air. The samples were denoted as MCr/SiO2 (M = Zr, Sr, Sn, and Ce) where the contents of promoter M and Cr were 2 and 10 wt %, respectively. The sample Cr/SiO2 with 12 wt % of Cr was also prepared by the same procedure as a reference.

4.2. Catalyst Characterization. The porosity of catalysts was analyzed on a Quantachrome Nova 1000e apparatus by measuring the nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K). The specific surface area, pore volume, and average pore diameter were calculated by the Brunauer–Emmett–Teller (BET) method and by the Barrett–Joyner–Halenda (BJH) method, respectively. The catalysts were degassed at 200 °C for 3 h prior to analysis.

The crystalline phase analysis was performed on a Bruker AXS D8 Advance diffractometer (Cu Kα, 40 kV, 40 mA, λ = 1.5406 Å). The diffraction patterns were recorded in the range from 10 to 80° with steps of 0.02°/s and an acquisition time of 2 s.

XPS was performed on a XSAM 800 spectrometer using Al Kα radiation (1486.6 eV) to obtain the surface chemical state and the atomic composition. The C 1s peak of adventitious carbon was fixed to 284.5 eV as a reference.

A UV2100 UV–visible spectrophotometer was used to measure the state of Cr species, and UV–vis diffuse reflectance spectra were scanned from 200 to 800 nm using BaSO4 as a sample holder.

The reducibility of the catalyst was studied on a TP-5080 apparatus equipped with a thermal conductivity detector (TCD). Typically, 50 mg sample was first pretreated in N2 flow (30 mL/min) at 300 °C for 3 h to remove the impurity, and then heated to 800 °C with a ramp of 10 °C/min in a H2–Ar mixture (5.0 vol % H2 in Ar).

CO2-TPD was used to analyze the basicity of the catalyst on a Micromeritics AutoChem II 2920 system equipped with a U-type reactor and a TCD. In a typical test, the sample was pretreated in He flow (50 mL/min) at 200 °C for 2 h, and then cooled down to 50 °C. The sample was exposed in diluted CO2 flow (50 mL/min, 10 vol % CO2 in He) until saturation which was determined by TCD. The desorption process was proceeded from 100 to 900 °C in He flow (50 mL/min) at a heating rate of 10 °C/min after purging the sample at 100 °C.

HAADF in a STEM mode was measured on an FEI Titan G2 60-300 (AC-TEM) apparatus combined with a Bruker Espir Super X detector, operating at 300 kV accelerating voltage.

TG analysis (NETZSCH STA 449 C) was employed to quantify the deposited coke on the spent catalyst, the combustion of coke was carried out from 100 to 700 °C in diluted oxygen flow (O2/N2: 10/90 vol) with a ramp of 5 °C/min.

4.3. Catalytic Evaluation. The catalytic oxidative dehydrogenation of ethane with carbon dioxide was carried out in a fixed-bed quartz reactor (i.d.: 8 mm, length: 200 mm) under atmospheric pressure. Usually, 300 mg of the catalyst mixed with 1.7 g quartz sand (40~60 mesh) was loaded in the middle of the reactor. The catalyst bed was heated to 700 °C in N2 flow (30 mL/min), and then switched to the reactants (C2H6/CO2/N2/Ar = 20:20:4:56, 30 mL/min). The gaseous products were analyzed by an online GC equipped with packed Porapak Q (3 mm o.d., 3 m length) and molecular sieve (3 mm o.d., 3 m length) columns in series and TCD. The conversion of reactants and the selectivity of products were calculated by:

\[
\text{Conversion} = \frac{n_{\text{in}} - n_{\text{out}}}{n_{\text{in}}} \times 100%
\]

\[
\text{Selectivity}_i = \frac{n_i}{\sum n_i} \times 100%
\]

The TOF was calculated by the following eq 5, where \( y \) represented the concentration of ethylene in the products, \( \dot{f}_{\text{total}} \) was the flow rate of the reactants in mol/s, and \( n_{\text{Cr}} \) was the amount of Cr in mole. The TOF was the following eq 5, where \( y \) represented the concentration of ethylene in the products, \( \dot{f}_{\text{total}} \) was the flow rate of the reactants in mol/s, and \( n_{\text{Cr}} \) was the amount of Cr in mole.

\[
\text{TOF (s}^{-1}) = \frac{y \dot{f}_{\text{total}}}{n_{\text{Cr}}}
\]

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