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Characterization of $Cu/CeO_2/\gamma\text{-}Al_2O_3$ thin film catalysts by thermal desorption spectroscopy

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Thermal desorption spectroscopy (TDS) under ultra high vacuum (UHV) condition has been used to investigate the desorption characteristics of $Cu/CeO_2/\gamma\text{-}Al_2O_3$ thin film catalysts coated onto the microchannel of a microreactor. TDS results demonstrate that surface desorption profiles and chemical properties (acid–base and redox properties) are remarkably influenced by the catalyst composition, i.e. the loading of copper and ceria. The enhanced basicity with the increase of ceria loading and the decrease of copper loading is evident from the shifted desorption maximum of CO_2 in TDS spectra. Three oxygen species, ranging from weakly bound oxygen desorbed at low temperature to the strongly held lattice oxygen desorbed at high temperature, are easily discernible and clearly identified by O_2 TDS spectra, depending on the catalyst compositions. The concomitant thermal desorption of O_2, CO_2, and H_2O at low temperature indicates the unique chemical properties of copper/ceria catalyst with appropriate copper and ceria contents. The observed low-temperature feature is ascribed to the role of porthole of copper/ceria interfacial area for several desorbed species. The weakly bound oxygen species is attributed to the enhanced abundance of copper/ceria interfacial anionic vacancies created by the intimate contact between copper and ceria entities and its impact on steam reforming of methanol (SRM) reaction is tentatively discussed in terms of reverse oxygen spillover.

KEY WORDS: steam reforming; Cu/CeO_2 catalysts; spillover; oxygen species; thermal desorption spectroscopy.

1. Introduction

Ceria and ceria-based materials have attracted considerable attention in environmental catalysis [1]. Ceria is a critical and multifunctional component of automotive emissions catalysts. It is well-known that ceria is not just an inert carrier for supported species, but also a modifier affecting the degree of dispersion as well as the redox behavior and catalytic activity of supported catalysts. While ceria may play a number of roles in enhancing the catalytic performance, its ability to store and release oxygen appears to be most significant, which allows catalyst to function efficiently under fuel rich and lean-burn conditions. The interaction of ceria with precious metals (Pd, Pt, Rh) and its effect on catalytic activity are well documented. Strong metal-support interaction (SMSI) discovered by Tauster *et al.* [2,3] was often claimed to interpret the observed promoting role of ceria [4,5].

In recent years, much research have been focused on the CuO/CeO_2 mixed oxide, because of the low cost of the base metal compared to the precious metals and the high catalytic efficiency of this catalyst for various reactions such as the combustion of CO and methane [6,7], the water–gas shift reaction [8], the reduction of SO_2 by CO [9], the methanol synthesis [10], steam reforming of methanol [11] and the wet oxidation of phenol [12]. A synergistic reaction pathway was proposed to explain the enhanced catalytic activity in CO oxidation, in which both the copper and ceria are simultaneously reduced or oxidized with CO or O_2 respectively [13]. It was speculated that interaction between copper and ceria plays an important role in promoting the catalytic activity. Concerning the nature of active sites of CuO/CeO_2 catalysts, it is generally accepted that these are related to well-dispersed copper oxide with an intimate contact with the ceria support. Correlation between the reducibility of CuO/CeO_2 and their catalytic activity appears to be well established. The reducibility of ceria has been studied extensively by temperature-programmed reduction (TPR). TPR has provided a great deal of practical information on the effect of dopants and pretreatment conditions on CuO/CeO_2 catalyst. However, the information is indirect as to how strongly the lattice oxygen is held in the CuO/CeO_2 catalyst materials. A much more direct measure would be oxygen desorption.

In this paper we report the thermal desorption spectroscopy (TDS) studies of $Cu/CeO_2/\gamma\text{-}Al_2O_3$ thin film catalysts under ultra high vacuum (UHV) condition; the goal is to investigate the influence of copper and ceria loading on thermal desorption profiles and to identify the oxygen species.

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2. Experimental section

2.1. Materials

$Cu/CeO_2/\gamma$-Al_2O_3 catalysts were prepared by a first alumina wash-coating followed by the subsequent impregnation of copper and cerium nitrate solutions. The detailed preparation method may be found elsewhere [14]. The microchannel substrate was first pretreated in air for 2 h at 1073 K. A suspension with a standard composition of 20 g γ-alumina (3 micro-APS powder, 99.97 purity, Alfa Aesar), 75 g water, 5 g binder polyvinyl alcohol (Fluka) and 1 g acetic acid was generated. The alumina powder and acetic acid were added successively, while stirring. The resulting suspension was stirred to remove air bubbles entrapped in the viscous mixture.

The alumina wash coats were filled into the etched channels of the stainless steel platelets using conventional wash coating methods. The washcoated platelets were then calcined in air for 2 h at a temperature of 873 K.

Before impregnation the wash coats (~15 mg) were evacuated in a desiccator connected to a vacuum pump for about 10 min to remove air from the pores. The evacuated pores were then filled by pure carbon dioxide at 0.5 bar. The wash-coated microchannels were then immersed into the mixed copper and cerium nitrates aqueous solutions with appropriate Cu/Ce ratio for impregnation of the active components. After impregnation with aqueous solutions of the desired molecular ratio of the copper and cerium nitrate, the impregnated wash coats were calcined for 2 h at 623 K in air. The total loading of copper and ceria was kept constant (~2 mg).

2.2. TDS measurements

Four samples were used in the present study as follows: γ-Al_2O_3, $Cu/CeO_2/\gamma$-Al_2O_3 (0.1), $Cu/CeO_2/\gamma$-Al_2O_3 (0.2), and $Cu/CeO_2/\gamma$-Al_2O_3 (0.6). The value in parentheses is the atomic ratio of copper to ceria.

TDS was performed under UHV condition. The catalyst platelet was carefully cut (~1×1 cm) and then transferred into an UHV chamber for surface analysis without any pre-treatment prior to the desorption measurement. TDS measurements were carried out in the UHV chamber (Leybold SSM 200, background pressure $\sim 3\times10^{-9}$ mbar) equipped with a quadrupole mass spectrometer (QMS). The temperature was programmed from 323 K to 973 K at a rate of 5 K/min after the initial stabilization of the temperature at 323 K and six selected ions ($m/q=2$, 17, 18, 28, 32, 44) were monitored simultaneously by QMS, corresponding toH_2^+, OH^+, H_2O^+,CO/N_2^+,O_2^+,CO_2^+, respectively.

3. Results and discussion

A TDS measurement was first carried out on the alumina thin film sample. The monitored MS intensity of the desorbed species was plotted versus ramped temperature, as shown in figure 1. Apparently water is the predominant desorption species on the alumina surface, indicating the highly hydrophilic nature of the alumina surface [15]. Three distinct desorption peaks were found to be centered at 478, 510, and 840 K respectively. Most of the water was released below 700 K. The concomitant desorption of the $m/q=17$ with water indicates that this species is the fragment of the water molecule. In addition to water, CO was the sec-

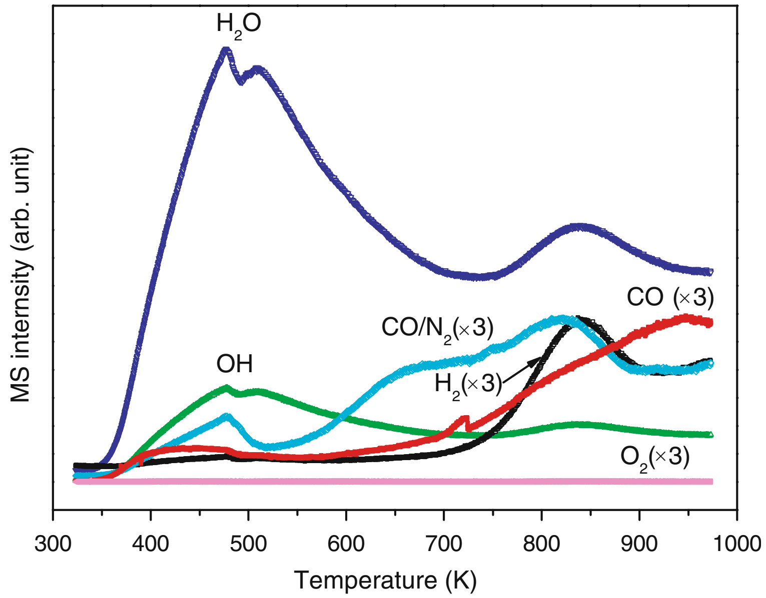

Figure 1. TDS spectra of γ-Al_2O_3 thin film.

ondary dominant species on the alumina surface. No apparent desorption feature of CO_2 was discerned on the alumina surface. The intensity of CO_2 was found to be much lower than that of CO. This experimental result can be understood by the fact of acidic nature of γ-alumina surface [16,17] and the acid–base interaction between CO and γ-alumina acidic surface.

TDS measurements were also carried out on the catalyst layers with different copper and ceria loading used in the microchannel reactor. TDS spectra of Cu/Ce = 0.6 with high copper loading are displayed in figure 2a. As can be seen from figure 2a, the addition of copper and ceria dramatically changes the TDS profile and CO_2 replaces CO to be the second major desorption species with a peak centered at 650 K. The growth of CO_2 is naturally ascribed to the addition of the basic oxide CeO_2 and CuO which may bond CO_2 to form carbonate or bicarbonate species. The non-concomitant CO desorption with CO_2 suggests that CO desorption peak arises from another species, instead of CO_2 fragmentation in the mass spectrometer. The fact that water is still the predominant species seems reasonable since alumina is the main component in the catalyst (88% weight percentage of the Cu/CeO_2/γ-Al_2O_3). Nevertheless, the water peaks become very broad and the desorption maxima are also shifted toward higher temperature, indicating the influence of the addition of copper and ceria on the desorption of water.

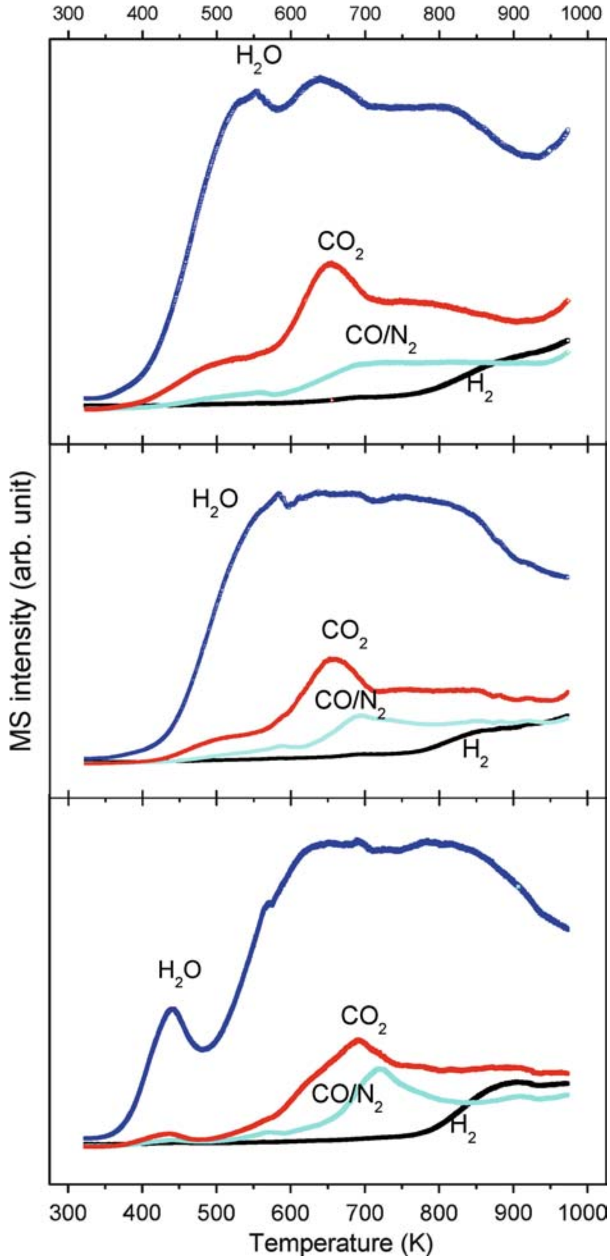

Figure 2. TDS spectra of Cu/CeO_2/γ-Al_2O_3 catalysts (a) Cu/Ce = 0.6; (b) Cu/Ce = 0.2; (c) Cu/Ce = 0.1 (from top to bottom).

The thermal desorption profile of catalyst with Cu/Ce = 0.2 was also checked out by TDS spectroscopy. As shown in figure 2b, the water desorption profile becomes even broader so that the desorption maxima are obscure and very difficult to be distinguished. It is noted that the CO_2 desorption maximum is shifted by 10 K to a higher value (~660 K). In the literature, the use of probe molecules for the characterization of oxide surface basicity is a well-adapted test [18]. Carbon dioxide, because of its acidity and of the large number of adsorbed species formed is often used as the probe molecule to measure surface basicity in numerous oxides [19,20]. The present observation is a clear evidence for the enhanced surface basicity with the increase of the ceria and the decrease of the copper loading.

Further measurements were carried out on the sample with an even lower copper loading ($CuO/CeO_2/\gamma$-Al_2O_3 with Cu/Ce = 0.1). As presented in figure 2c, the further decrease of copper loading gives some new features in the low temperature range and the CO_2 desorption maximum is further shifted to around 690 K, indicating the further enhanced surface basicity. It appears that the first desorption maximum of water at 550 K (figure 2a, Cu/Ce = 0.6) is lowered to 435 K. This result demonstrates that the variation of the copper and ceria ratio may remarkably alter the chemical properties of $Cu/CeO_2/\gamma$-Al_2O_3 catalysts.

In a paper dealing with CO_2 adsorption and desorption on ceria, two desorption peaks were assigned to monodentate and bidentate carbonate species [21]. Contrary to that study, only a high temperature feature was found in CO_2 TDS experiment of $Cu/CeO_2/\gamma$-Al_2O_3 catalysts with Cu/Ce 0.6 and 0.2. The disappearance of the CO_2 low temperature feature might be the result of the calcinations of the sample at 623 K. Whereas the concomitant desorption of carbon dioxide and water in the low temperature range in figure 2c (Cu/Ce = 0.1) demonstrates the impact of the variation of copper and ceria loading on the surface desorption profile.

Desorption features of hydrogen were found at the high temperature over alumina and three $Cu/CeO_2/\gamma$-Al_2O_3 catalysts, indicating the presence of the hydride species at high temperature. A density functional theory (DFT) calculation predicted the existence of varying amounts of hydrogen in bulk alumina to reconcile inconsistent experimental data [22]. Besides, the interaction of hydrogen with ceria-based oxides has also been studied in detail by nuclear magnetic resonance (NMR) [23], electron spin resonance (ESR), X-ray diffraction (XRD) [24] and first-principle calculation [25], indicating the incorporation of hydrogen in the ceria lattice. This may rationalize the high-temperature hydrogen released from all samples. Nevertheless this high-temperature feature is not the main concern of this study.

Cu/CeO_2 catalysts have received considerable interest in the past years due to their excellent catalytic activity for steam reforming of methanol (SMR) reaction [11,26,27]. Despite these studies, the active sites of Cu/CeO_2 catalysts and the role of ceria support for SRM reaction are not well understood. Recently we reported a parallel screening methodology of $Cu/CeO_2/\gamma$-Al_2O_3 catalysts for SRM reaction in a 10-channel microreactor [14]. The dependence of the catalytic activity on Cu/Ce ratio shows clearly a monotonous increase of catalytic activity with the decrease of the copper loading. A reaction mechanism was proposed to rationalize the catalytic activity data and characteristics of the catalysts, which supposes that the copper/ceria interfacial area (partially oxidized copper nanoparticle and defective ceria) is the active site for steam reforming of methanol (see figure 3). The SRM reaction over $CuO/CeO_2/\gamma$-Al_2O_3 catalysts is considered to follow a redox mechanism. For the methanol synthesis reaction, the reverse reaction of the steam reforming of methanol, the surface oxygen was seen as important in the mechanism of methanol synthesis both as intermediate and promoter [28,29]. Since the surface oxygen species play an important role in redox catalysis [30], the oxygen TDS spectra are presented in detail in figure 4 despite their low intensity compared to other species.

The information from O_2 TDS spectra is quite straightforward. It is very interesting to notice that the oxygen desorption profile is strongly dependent on the catalyst composition, i.e. copper and ceria loading. In contrast to two oxygen species over Pt/CeO_2 catalyst reported in the literature [31], three oxygen species are clearly identified on $Cu/CeO_2/\gamma$-Al_2O_3 catalysts by using O_2 TDS spectra, ranging from weakly bound oxygen desorbed at low temperature to strongly held lattice oxygen desorbed at high temperature. Recently, TPR by hydrogen (H_2-TPR) has been carried out to identify the surface oxygen species over Cu–Ce–O mixed oxide

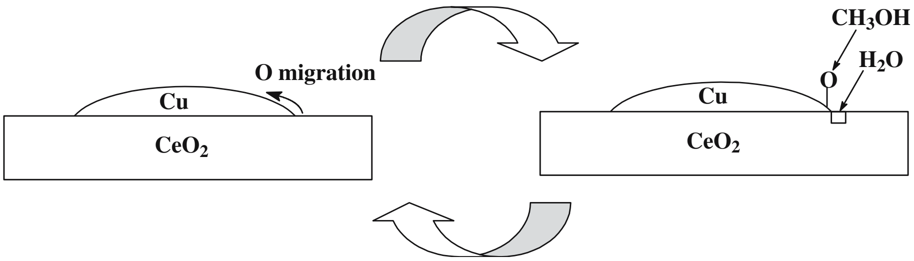

Figure 3. Proposed SRM reaction mechanism at Cu/Ce boundary.

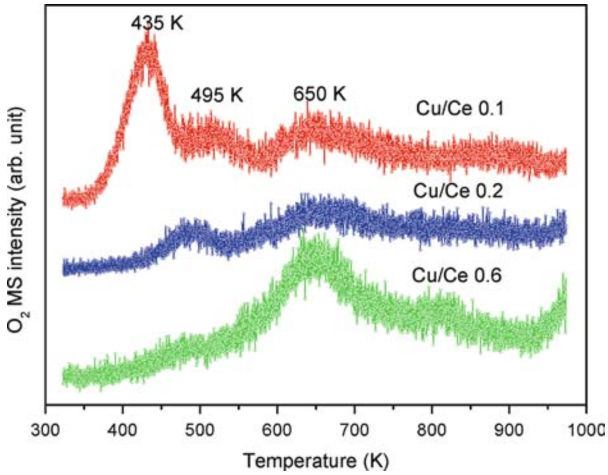

Figure 4. Influence of copper loading on O_2 thermal desorption profile.

Table 1
Thermal desorption parameters of TDS spectra over $Cu/CeO_2/\gamma$-Al_2O_3 catalysts

Parameters	Cu/Ce = 0.6	Cu/Ce = 0.2	Cu/Ce = 0.1
$T_{\max}{}^{a}$ CO_2	650	660	690/435
$T_{\max}$ CO	690	700	725/435
$T_{\max}$ O_2	650	650/495	650/495/435[c]
$CO/CO_2{}^{b}$	0.3	0.5	0.8

[a] $T_{\max}$ is the temperature (K) where the maximum desorption rate is found.
[b] intensity ratio of CO to CO_2 in the desorption peak.
[c] is the indication of multiple desorption peaks for the identical species.

without alumina. Li *et al.* [32] used H_2-TPR to identify three oxygen species similar to our direct observation by TDS. Some discrepancies still exist, e.g. the absence of the first oxygen desorption peak in our TDS results (Cu/Ce = 0.2), which was found in Li's study. This may be explained by the different catalyst preparation method and the difference in the characterization method. It should be stressed that TDS offers a unique advantage over conventional H_2-TPR in that a small amount of sample (active component copper and ceria < 0.5 mg) and a sample with a more flexible geometry is allowed for measurement. Moreover, TDS is a much more direct measure for the determination of oxygen species as compared to H_2-TPR.

In consideration of the fact that the SRM reaction with $Cu/CeO_2/\gamma$-Al_2O_3 catalysts were generally carried out at temperature below 573 K, it is important to study the nature of oxygen species on the surface and their roles in catalytic reactions at low temperature. Correlating the TDS features and the catalytic activity, the low temperature feature and enhanced surface basicity appear to favor the higher catalytic activity. Duprez and coworkers [33] found a good correlation between the surface oxygen mobility and the metal–oxygen bond strength in the oxide except for ceria. The authors attributed the large amount of CO_2 chemisorbed on ceria to the presence of oxygen vacancies by the correlation between basicity and the oxygen mobility. In the present contribution, the CO_2 desorption feature at the high temperature may be less important since their desorption temperature is much higher than the reaction temperature of 523 K. The concomitant desorption of O_2, CO_2, and H_2O on catalyst with Cu/Ce = 0.1 indicates that the low temperature feature may arise from the decomposition of the same species or the same surface sites with the similar thermal reactivity. This low temperature desorption feature is likely the crucial factor to control the catalytic activity. All the desorption maxima of CO_2, O_2, and CO are summarized in table 1. The relative ratios of CO to CO_2 are also included for comparison. Apparently, the smaller the Cu/Ce ratio is, the larger the value of CO/CO_2 was found. One possible explanation behind this observation is speculated that CO_2 inserts one oxygen to fill one oxygen vacancy and consequently desorbs as CO at high temperature. In a previous study, White *et al.* [34] suggested the formation of CO in the TPD of CO_2 from Pt/CeO_2 catalyst was caused by the donation of oxygen in CO_2 to a lattice vacancy at the interface to produce CO. Therefore, the ratio of CO to CO_2 may somehow reflect the population of surface defects. However this postulation need to be further justified and proved by more experimental evidences.

O_2-TDS gives valuable information on oxygen available from the catalyst surface, mainly related to copper particles and their very close vicinity. The oxygen desorbed at high temperature is attributed to the oxygen strongly held in the lattice of ceria and copper oxide. The relative ease of oxygen removal in $Cu/CeO_2/\gamma$-Al_2O_3 catalysts may be the result of the presence of grain boundaries and defects, which are also known to increase the rate of oxygen diffusion through ceria [34–36]. The weakly bound adsorbed oxygen species desorbed in the low temperature range is ascribed to the enhanced surface anionic vacancies located in the copper and ceria interfacial area, which are created by the intimate contact between small copper nanoparticle and ceria support. The oxygen adsorbed on the vacancies in the close vicinity of copper particle is highly mobile and active at the low temperature of the SRM reaction. Gorte *et al.* [37] reported the oxygen transfer from ceria to Rh evidenced by the temperature programmed desorption of CO and steady-state CO oxidation rates. Following these arguments, the observed weakly bound and labile oxygen is suggested to reverse spillover to oxidize the reduced copper surface, which is likely essential for the chemisorption of methanol on copper entities, although the oxygen coverage might be limited to half monolayer or less. This reaction model also seems compatible with a recent proposal about the role of strain on SRM reaction over binary Cu/ZnO catalysts [38]. Lattice expansion of Cu resulting from facile oxygen migration from ceria to copper may cause a significant strain on the copper surface [39] and, thus, improve methanol chemisorption [40–42] and promote the catalytic activity.

Under certain circumstance, the copper and ceria interfacial area may serve as the porthole not only for O_2, but also for CO_2 and H_2O. This rationalizes the concurring of thermal desorption of O_2, CO_2, and H_2O at low temperature. This finding was not observed in the precious metal/ceria catalyst system, implying the unique chemical properties and copper/ceria interaction. More anionic vacancies are created by the intimate contact of copper and ceria when copper loading is lowered to a copper to cerium ratio of 0.1. This explains why the catalysts with Cu/Ce = 0.1 and Cu/Ce = 0.2 are more catalytically active than other catalysts.

Obviously, much work will be needed to answer questions about the nature of the oxygen species and copper and ceria support interaction.

4. Conclusions

Thermal desorption spectroscopy was proven to be a very efficient tool for the investigation of the characteristics of $Cu/CeO_2/\gamma\text{-}Al_2O_3$ thin film catalysts coated on the microchannels. TDS results presented clearly demonstrate that the variations in the chemical composition of $Cu/CeO_2/\gamma\text{-}Al_2O_3$ catalysts alter markedly the surface desorption profiles and chemical properties (acid–base and redox properties) on the catalyst surface. The shifted desorption maximum of temperature programmed desorption of CO_2 provides evidence for the enhanced basicity with the increase of the ceria and the decrease of the copper contents. One the other hand, three oxygen species, ranging from weakly bound oxygen desorbed at low temperature to the strongly held lattice oxygen desorbed at high temperature, are clearly identified over $Cu/CeO_2/\gamma\text{-}Al_2O_3$ thin film catalysts, depending on the catalyst composition. The concomitant thermal desorption of O_2, CO_2, and H_2O at low temperature indicates the unique chemical properties of copper/ceria catalyst with appropriate copper and ceria contents and role of porthole of copper/ceria interfacial area for several desorbed species. The observed low temperature feature and weakly bound oxygen species attributable to the enhanced surface anionic vacancies created by the intimate contact between copper and ceria entities is suggested to be correlated with the catalytic activity of steam reforming of methanol reaction.

Acknowledgments

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