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Review (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

The application of incorporation model in γ - Al_2O_3 -supported single and dual metal oxide catalysts: A review

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ARTICLE INFO

Article history:

Received 31 August 2013

Accepted 10 September 2013

Published 20 November 2013

Keywords:

 γ -Alumina support

Supported metal oxide catalyst

Surface interaction

Incorporation Model

Surface synergetic oxygen vacancy

ABSTRACT

The investigation of the interaction between the surface dispersed components and the supports is the key to understand the nature of catalytic reactions. A single metal oxide (CuO) and dual metal oxides ($\text{CuO-Mn}_2\text{O}_3$, CuO-CoO , etc.) were supported on γ - Al_2O_3 to produce model catalysts. The dispersion behavior of these metal oxides on the surface of γ - Al_2O_3 and some physicochemical properties were explained using the Incorporation Model. These properties were considered together with their catalytic performances in $\text{CO}+\text{O}_2$ and $\text{NO}+\text{CO}$ model reactions to explore “composition-structure-property” relationships. A possible reaction mechanism involving surface synergetic oxygen vacancy on the supported dual metal oxide catalysts was proposed to approach the nature of NO reduction by CO .

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1. Introduction

The study of the supported metal oxide catalysts is a hot topic in heterogeneous catalysis because these catalysts are used in many important industrial reactions ($\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst for the partial oxidation of methane to syngas [1–3], $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts for the oxidative dehydrogenation of propane [4,5], etc.). The physicochemical properties and catalytic performance of supported metal oxide catalysts are influenced by the dispersion state and the loading of the metal oxide, as well as the surface structure of the support. The investigation of the surface interaction between the surface dispersed components and the supports is very significant to understand the nature of these catalytic reactions and prepare efficient and practical catalysts.

As early as 1951, Professor Selwood at California University pointed out that: for supported metal oxide catalysts, the sup-

port is not just an inert material, but that it often affects the nature of the surface dispersed components [6]. Investigating the nature of the interaction between the surface dispersed components and the supports not only benefits the understanding of the structure, distribution, and strength of the surface active sites of the catalysts and the catalytic reaction mechanism, but it is also an essential condition for the scientific design and preparation of this kind of catalysts. For example, a sulfurized $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst was widely used in many industrial catalytic hydrodesulfurization (HDS) processes due to its good catalytic performance [7–9]. Several models to describe the surface interaction of the catalyst were discussed by Massoth in 1978 [10]. In detail, these models are as follows.

(A) Monolayer Model. In 1969, Lipsch et al. [11] proposed the Monolayer Model. They believed that an epitaxial monolayer of MoO_3 was formed on the surface of $\gamma\text{-Al}_2\text{O}_3$ in the catalyst preparation process. However, this was just a hypothesis at

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This work was supported by the National Natural Science Foundation of China (20873060, 20973091), the National Basic Research Program of China (973 Program, 2010CB732300), and Jiangsu Science and Technology Support Program (SBE201100389).

DOI: 10.1016/S1872-2067(12)60708-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 11, November 2013

that time, which received definitive evidence only after the experiment results of Sonnemans et al. [12]. Jacono et al. [13] have carried out a specialized discussion of the structures and existing states of the additive (Co) and confirmed that these ions entered tetrahedral and octahedral vacancies on the surface of $\gamma\text{-Al}_2\text{O}_3$, and Co^{2+} occupied the tetrahedral vacancy preferentially.

(B) Intercalation Model. The Intercalation Model was proposed by Beer and Schuit [14]. They believed that the oxide monolayer was damaged and the separated MoS_2 crystallites were formed in the sulfurization process. The inserted CoMoS_2 can be formed by the reaction between the additive (Co) and MoS_2 . The other important role of Co is beneficial to generate small crystallites of MoS_2 in the sulfurization process. Furthermore, Co can promote the formation of Mo^{3+} because it occupies the edge position in the MoS_2 crystallite, while Mo^{3+} is considered to be the active site of the catalyst. If Co is absent, the concentration of Mo^{3+} will be reduced, which leads to the decrease of the catalytic performance. The support was considered as just a diluent in the Intercalation Model.

(C) Contact Synergism Model. This model was proposed by Hagenbach et al. [15,16]. They confirmed that a mixture of MoS_2 and Co_9S_8 had a significant synergistic effect, that is, Co_9S_8 had almost no activity, but when it was added into MoS_2 , it would significantly increase the activity of MoS_2 for the hydrodesulfurization of thiophene, cyclohexene hydrogenation, ring hexane isomerization, and other reactions. An acceptable explanation for the synergistic effect is that electron transfer between adjacent MoS_2 and Co_9S_8 , as well as the additional electron transfer resulted from the excess sulfur promote the enhancement of the catalytic activity remarkably. In summary, the Contact Synergism Model considered that the catalytic performance of the sulfide compound was better than that of the single component, while the support had no significant impact on the catalytic performance.

As Massoth said in his comment [10], each of the above models has some experiment data to support it, and these models provide an intuitive picture for researchers to understand the nature of the catalyst and the role of additives, but they are not universal. For example, one model often can be used for one system, but it is not good for another system and can even contradict its experimental results. It was also noted that these models qualitatively explained the role and generation of the active components, but they did not describe the results in a quantitative way. Furthermore, the Intercalation Model and Contact Synergism Model also ignored the interaction between surface dispersed components and the supports, which seriously limits the universality of these models.

With the development of surface characterization techniques, Professors Xie and Tang at Peking University found that a series of ionic compounds (oxides and salts) were able to disperse spontaneously on the surface of the supports to form a monolayer [17]. They proposed the Surface Close Packed Monolayer Model to calculate the dispersion capacities of the dispersed ionic compounds. The basic idea of this model is that the dispersion capacities of ionic compounds on the surface of supports can be determined by the two dimensional close

packed anions, that is, the dispersion capacities are the numbers of anions piled up along the two-dimensional directions of the monolayer on the surface of supports. The model is very good for calculating the dispersion capacities of MoO_3 , WO_3 , La_2O_3 , Fe_2O_3 , etc. on some metal oxide supports (such as $\gamma\text{-Al}_2\text{O}_3$), but for many divalent metal oxides (such as CuO , NiO , ZnO , MgO , and CdO) and many salts (such as NaCl , KCl , CuCl , CuCl_2 , and other halides), there are large deviations between calculated values and experimental results.

Since the early 1990s, on the basis of the analysis of a large number of experimental results and relevant data reported in the literatures, Professor Chen and coworkers [18,19] proposed the Incorporation Model to describe the interaction between surface dispersed components and supports by considering the surface structure of supports and the nature of surface dispersed components. This model has five fundamental aspects: (1) existence of appropriate vacancies on the surface of the supports that allows the supports to act as the framework for the spontaneous dispersion of the ionic compounds; (2) the dispersion of supported ionic compounds on the surface of the supports is based on the incorporation of their cations into surface vacancies, while keeping associated anions in close proximity to maintain electric neutrality; (3) the dispersion capacities of different valence-type ionic compounds, such as 1-1, 1-2, 2-1, 1-3, and 2-3 valence pairs, can vary because of the different shielding effects produced by the accompanying anions; (4) different supports have different types of surface vacancies (tetrahedral, octahedral, and cubic), and the same support can have more than one kind of vacancy (e.g., both tetrahedral and octahedral vacancies exist on the surface of $\gamma\text{-Al}_2\text{O}_3$), and it is necessary to consider the steric or preferential effect when discussing the incorporation of cations into vacancies (a relationship between cation radius and vacancy size, as well as the stability of the coordination); (5) the shielding effects of the same anion will be different on supports with different surface vacancy densities, and when the anionic shielding effect increases to a certain degree, a surface close packed monolayer is formed. This model quantitatively explains the dispersion capacities of different valence-type metal oxides (such as Li_2O , NiO , CuO , MoO_3 , etc.) on a number of metal oxide supports ($\gamma\text{-Al}_2\text{O}_3$, CeO_2 , TiO_2 , ZrO_2 , etc.). It also explains why different metal oxides on the same support have different dispersion capacities and why the same metal oxide exhibits different dispersion capacities on different supports. In addition, it explains why low valence metal oxides do not form a surface close packed monolayer on the surface of metal oxide supports.

In the present work, $\gamma\text{-Al}_2\text{O}_3$ is used as the support for a single metal oxide (CuO) and dual metal oxides ($\text{CuO-Mn}_2\text{O}_3$ and CuO-CoO) to prepare model catalysts. This work is mainly focused on: (1) using the basic ideas of the Incorporation Model to explain the dispersion capacities and physicochemical properties of the surface dispersed components; (2) propose a reaction mechanism involving surface synergetic oxygen vacancy (SSOV) by characterizing their physicochemical properties and catalytic performance in $\text{CO}+\text{O}_2$ and $\text{NO}+\text{CO}$ model reactions before and after CO pretreatment, to explain the promotion effects of Mn_2O_3 and CoO . Based on the exploring and under-

Fig. 1. Schematic diagram of γ - Al_2O_3 crystal. Spheres 1 and 2 representing O^{2-} ions, sphere 3 standing tetrahedral vacancy, and sphere 4 denoting octahedral vacancy [20].

standing of the composition-structure-property relationships of the supported metal oxide catalysts, we hope to provide a scientific basis to improve and develop high efficiency supported metal oxide catalysts.

2. Surface interaction and catalytic performance of γ - Al_2O_3 -supported single metal oxide catalyst (CuO/γ - Al_2O_3)

γ - Al_2O_3 is widely used as a support because of its large specific surface area and good stability, and O^{2-} arranged as cubic close packed in its “defect spinel” structure (Fig. 1) [20]. Its preferentially exposed plane is (110), which has C-Layer and D-Layer arrangements, as shown in the gray plane of Fig. 1. It is arranged as CDCDCD....., so the exposed opportunities of C-Layer and D-Layer are equal [20–22]. Some tetrahedral (Tet) and octahedral (Oct) vacancies exist in the O^{2-} close packed structure, and Al^{3+} ions fill some of Tet and Oct vacancies. The C-Layer and D-Layer of the γ - Al_2O_3 (110) plane are simplified to a planar model in Fig. 2. A rectangle in the figure represents the unit mesh of the γ - Al_2O_3 (110) plane (constitutional unit). Half of the Al^{3+} ions occupy Tet vacancies, and the other half exist in Oct vacancies in C-Layer, while all the Al^{3+} ions locate in the Oct vacancies in D-Layer. At the same time, there are the same numbers of vacancies in C-Layer and D-Layer within a unit mesh, including 8 Tet vacancies and 4 Oct vacancies. In C-Layer, Al^{3+} ions occupy 2 Tet vacancies and 2 Oct vacancies, while Al^{3+} ions only occupy 2 Oct vacancies in D-Layer. The approximate area of a unit mesh is 0.443 nm^2 (O^{2-} radius is 0.14 nm), which

Fig. 2. Planar structure diagram of C-Layer and D-Layer of the γ - Al_2O_3 (110) plane [20,23].

can be calculated from Fig. 2. The C-Layer has 8 unoccupied vacancies per mesh. The D-Layer possesses 10 unoccupied vacancies per mesh. The unoccupied vacancy density on the surface of γ - Al_2O_3 is $3.375 \text{ mmol}/100 \text{ m}^2$, of which unoccupied Oct vacancies are $0.75 \text{ mmol}/100 \text{ m}^2$. These unoccupied vacancies (Tet and Oct vacancies) provide space for the dispersion of metal cations. When cations enter unoccupied vacancies (simply denoted as vacancies below), the accompanied O^{2-} ions are located on them to maintain electric neutrality. The shielding (or steric) effect for a neighbor vacancy is different due to differences in the valence and the number of accompanying O^{2-} ions around each dispersed cation. For a dispersed low valence metal oxide, such as CuO , each incorporated Cu^{2+} ion is accompanied by only one O^{2-} ion (capping oxygen ion), and the capping oxygen ion does not produce a shielding effect for the neighbor vacancy on the (110) plane of γ - Al_2O_3 . When all the Oct vacancies are occupied by dispersed Cu^{2+} ions, the accompanying O^{2-} ions do not form an oxygen close packed monolayer. For a dispersed high valence metal oxide, such as MoO_3 , each dispersed Mo^{6+} ion is accompanied by three O^{2-} ions, which makes the neighbor vacancy partly or completely shielded, and an oxygen close packed monolayer is formed when just part of the surface vacancies are occupied by dispersed Mo^{6+} ions [23,24]. In our previous several review articles [25–28], the dispersion of different valence metal oxides on different metal oxide supports with different structures was discussed. Here, we mainly take γ - Al_2O_3 -supported single metal oxide (CuO) for studying, and deeply investigate the difference in the nature of the CuO/γ - Al_2O_3 catalysts before and after CO pretreatment, and further explain the dispersion and catalytic performance of CuO on the surface of γ - Al_2O_3 by the Incorporation Model.

As well known, the dispersion capacity of CuO on the surface of γ - Al_2O_3 is $0.75 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma$ - Al_2O_3 (denoted as $0.75\text{Cu}/\text{Al}$, same below) after 450 – 500°C calcination. This is consistent with the octahedral vacancy density on the γ - Al_2O_3 (110) surface [29]. H_2 temperature-programmed reduction (H_2 -TPR) profiles (Fig. 3) show that Cu^{2+} ions in $0.3\text{Cu}/\text{Al}$ sample (reduction peak temperature is 247°C) are more difficult to be reduced than those in $0.6\text{Cu}/\text{Al}$ sample (reduction peak temperature 207°C). Comparing the reduction peak shape of

Fig. 3. H_2 -TPR profiles of various Cu/Al samples [30].

Fig. 4. Schematic diagram for dispersed copper oxide species on the (110) plane of γ - Al_2O_3 [30].

the two samples, the reduction peaks of 0.6Cu/Al sample are considered as the superposition between the reduction peak of 0.3Cu/Al sample and another new peak. Combined with Incorporation Model, a possible explanation is that when CuO is dispersed on the surface of γ - Al_2O_3 , Cu^{2+} ions preferentially occupy the octahedral vacancies in C-Layer to form a stable six-coordinated octahedral structure. Continue to increase copper oxide loading, Cu^{2+} ions gradually occupy octahedral vacancies in D-Layer to form a relatively unstable five-coordinated missing corner octahedral structure (Fig. 4) after occupying all the octahedral vacancies of C-Layer. The incorporated Cu^{2+} ions in D-Layer are more easily attacked by hydrogen and get reduced. Therefore, there are two different coordination environments for dispersed copper species on the surface of γ - Al_2O_3 , i.e., the six-coordinated octahedral structure in C-Layer and unstable five-coordinated missing corner octahedral structure in D-Layer [30].

The catalytic performance of Cu/Al samples for CO+ O_2 reaction at different reaction temperatures is shown in Fig. 5. It shows that the catalytic performance of 0.6Cu/Al sample is obviously better than that of 0.3Cu/Al sample. This is related to the asymmetric extent of the coordination environment of the copper species on the surface of γ - Al_2O_3 . It is noteworthy that the catalytic performance of the Cu/Al samples is further increased dramatically after CO pretreatment.

It is well known that abundant surface oxygen vacancies (SOVs) can be generated on the surface of the supported metal oxide catalysts by reduction pretreatment at a suitable temperature, which play an important role in the activation of O_2 and NO molecules in the catalytic reactions of CO oxidation and

NO elimination [31–33]. The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results showed that low valence copper species were generated on the surface of CuO/ γ - Al_2O_3 sample after the CO pretreatment at 250 °C (denoted as Cu/Al-CO, same below) [30]. Taking C-Layer of the γ - Al_2O_3 (110) plane as an example, it is known from Incorporation Model (Fig. 6) that the CO pretreatment lets CO capture the O of Cu^{2+} -O- Cu^{2+} to form $\text{Cu}^+-\square-\text{Cu}^+$ structure ($\square$ represents SOV). In addition, Cu^+ ions can easily adsorb CO molecules [34–36] and the SOV is beneficial for activating O_2 molecules, so the catalytic performance of Cu/Al-CO samples is improved significantly.

3. Surface interaction and catalytic performance of γ - Al_2O_3 -supported dual metal oxide catalysts (CuO/ Mn_2O_3 / γ - Al_2O_3 and CuO-CoO/ γ - Al_2O_3)

The CuO/ γ - Al_2O_3 catalyst is considered as a potential substitute for the traditional noble metal three-way catalyst (TWC) due to its excellent activity for the catalytic reduction of NO by CO and good thermal stability. However, its activity and selectivity at low temperatures are still unsatisfactory. Therefore, some additives (mainly fourth period transition metal oxides) are added to change the surface coordination states of the supported copper species, and increase the interaction between copper species and additives, which are conducive for improving catalytic performance. In the present work, γ - Al_2O_3 -supported dual metal oxide catalysts (CuO/ Mn_2O_3 / γ - Al_2O_3 and CuO-CoO/ γ - Al_2O_3) have been prepared and studied by a series of characterization techniques. Combined with Incorporation

Fig. 5. Influence of CO pretreatment on the activity of Cu/Al samples for the total oxidation of CO at different temperatures [30].

Fig. 6. Schematic diagram for dispersed copper oxide species on the (110) plane of $\gamma\text{-Al}_2\text{O}_3$ (C-Layer) before and after CO pretreatment [30].

Model, the surface structure of the catalysts and their catalytic performance are associated to discuss the structure-activity relationship of the catalysts. Some research results about the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst modified with the fourth period transition metal oxides (Mn_2O_3 and CoO) obtained by our research group in recent years are summarized here. Some related research on other metal oxides (such as CeO_2 , MgO , and TiO_2) modifying $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts have been reported in our previous review in detail [26].

Previous studies indicated that the introduction of variable valence transition metal oxides (such as Mn_xO_y , Co_xO_y , etc.) as a modifying additive into the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ system can improve

the catalytic performance, but the investigation of the interaction between the modifying oxide and CuO is not very deeply [37,38]. Therefore, $\text{CuO}/\text{Mn}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ model catalysts were prepared by stepwise impregnation method to investigate the influence of Mn_2O_3 on the reduction behavior of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ and the dispersion of CuO on the surface of $\gamma\text{-Al}_2\text{O}_3$. Furthermore, the corresponding catalytic performance for $\text{NO}+\text{CO}$ reaction was tested [39]. The XRD and XPS results confirm that manganese oxide and copper oxide species on the surface of $\gamma\text{-Al}_2\text{O}_3$ are in the forms of Mn_2O_3 and CuO , respectively [39]. XRD results (Fig. 7 and Fig. 8) indicate that the dispersion capacity of Mn_2O_3 on the surface of $\gamma\text{-Al}_2\text{O}_3$ is 1.0 mmol $\text{Mn}^{3+}/100$

Fig. 7. XRD patterns (a) and quantitative XRD results (b) of Mn/Al samples with different loadings [39].

Fig. 8. XRD patterns (a) and quantitative XRD results (b) of $\text{xCu}/1.0\text{MnAl}$ samples with different loadings of CuO [39].

$\text{m}^2 \gamma\text{-Al}_2\text{O}_3$, while the dispersion capacity of CuO on $\gamma\text{-Al}_2\text{O}_3$ support modified by Mn_2O_3 is $1.1 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$.

In the previous section, it has been mentioned that the dispersion capacity of CuO on $\gamma\text{-Al}_2\text{O}_3$ support is $0.75 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$ [29], while the dispersion capacity of CuO on the surface of $\gamma\text{-Al}_2\text{O}_3$ modified by Mn_2O_3 ($1.0 \text{ mmol Mn}^{3+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$) increases to $1.1 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$. Incorporation Model is used to analyze the reason. It is well known that Mn_2O_3 has several kinds of crystal forms (α , β , and γ), while the crystal form of $\gamma\text{-Mn}_2\text{O}_3$ is the same as $\gamma\text{-Al}_2\text{O}_3$. Assuming that the dispersion of Mn_2O_3 on the surface of $\gamma\text{-Al}_2\text{O}_3$ is by the epitaxial growth method, then this can lead to the increase of the dispersion capacity of CuO. When the calcination temperature is below 750°C , it is difficult for Cu^{2+} to occupy the tetrahedral vacancy of $\gamma\text{-Al}_2\text{O}_3$, while according to the literature [40], Cu^{2+} can enter the tetrahedral vacancy of Mn_2O_3 . So the

dispersion capacity of CuO on the surface of $\gamma\text{-Al}_2\text{O}_3$ modified by Mn_2O_3 is increased. Accordingly, it is believed that the dispersion of Mn_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ support is in the epitaxial growth mode. As mentioned above, for the preferentially exposed plane of $\gamma\text{-Al}_2\text{O}_3$, the exposed opportunities of C-Layer and D-Layer are numerically equal. The epitaxial growth of Mn_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ is that the original C-Layer covered by the D-Layer growth, whereas the original D-Layer covered by the C-Layer growth. To provide a better understanding of the dispersion of Mn_2O_3 and CuO on the surface of $\gamma\text{-Al}_2\text{O}_3$, the C-Layer of $\gamma\text{-Al}_2\text{O}_3$ is given as an example in the schematic view shown in Fig. 9. Therefore, it can be considered that Cu^{2+} ions occupy the tetrahedral vacancies of Mn_2O_3 , which leads to the increase of the dispersion capacity of CuO. The results of NO+CO reaction (Fig. 10) indicate that Mn_2O_3 can promote the dispersion of CuO and the shift of $\text{Cu}^{2+} + \text{Mn}^{3+} \leftrightarrow \text{Cu}^{+} + \text{Mn}^{4+}$ redox equilibrium, as well as

Fig. 9. The diagram for the dispersion of copper oxide on the surface of $\gamma\text{-Al}_2\text{O}_3$ and Mn_2O_3 modifying $\gamma\text{-Al}_2\text{O}_3$ [39].

Fig. 10. Catalytic performance of xCu/yMnAl catalysts for NO+CO reaction at different operation temperatures [39].

Fig. 11. Schematic diagram for dispersed CoO species (a), dispersed CuO species (b), and both dispersed CuO and CoO species (c) on the (110) plane of γ -Al₂O₃ [C-Layer] [41].

the enhancement of the adsorption of NO₂ (reaction intermediate species), which further improve the catalytic performance remarkably.

In addition, CuO-CoO/ γ -Al₂O₃ model catalysts were prepared by co-impregnation method [41]. According to the literatures [13,42], Co²⁺ ions preferentially enter the tetrahedral vacancies of γ -Al₂O₃, while Cu²⁺ ions preferentially occupy the octahedral vacancies. It can be seen from Incorporation Model that Co²⁺ in a tetrahedral vacancy shares a capping oxygen with the adjacent Cu²⁺ in octahedral vacancy to form Cu²⁺-O-Co²⁺ species (Fig. 11). H₂-TPR results (Fig. 12) further confirm the existence of Cu²⁺-O-Co²⁺ species and that its reduction was significantly more facile than Cu²⁺-O-Cu²⁺ and Co²⁺-O-Co²⁺ species. The excellent reduction behavior of CuO-CoO/ γ -Al₂O₃ catalysts is beneficial to the formation of low valence copper species in NO+CO reaction process, which promotes the enhancement of the catalytic performance (Fig. 13).

4. Influence of CO pretreatment on the catalytic performance of γ -Al₂O₃-supported dual metal oxide catalysts (CuO-Mn₂O₃/ γ -Al₂O₃ and CuO-CoO/ γ -Al₂O₃)

In the second section, it has been mentioned that CuO/

Fig. 12. H₂-TPR profiles of 0.2Cu0.6Co/Al-Air, 0.6Co/Al, and xCu0.6Co/Al catalysts with different copper oxide loadings [41].

γ -Al₂O₃ catalyst after CO pretreatment will generate abundant surface oxygen vacancies (SOVs) and low valence Cu⁺ species, which are conducive for enhancing catalytic performance. In recent years, we find that the catalytic performance of some supported CuO-M_xO_y dual metal oxide catalysts after an appropriate reduction treatment is significantly better than the two corresponding single metal oxide catalysts with the same treatment [43,44]. On the basis of this, the concept of surface synergetic oxygen vacancy (SSOV) is proposed and the variation of the catalytic performance of these catalysts brought by the reduction treatment is successfully explained.

The supported bi-component model catalyst with copper ox-

Fig. 13. NO conversion (a) and N₂ selectivity (b) over 0.2Cu/Al, 0.6Cu/Al, 0.6Co/Al, 0.2Cu0.6Co/Al-Air, and xCu0.6Co/Al catalysts with different copper oxide loadings as a function of reaction temperature [41].

ide and manganese oxide ($\text{CuO-Mn}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$) has been prepared by the co-impregnation method. The loadings of Cu^{2+} and Mn^{3+} are $0.6 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$ and $0.3 \text{ mmol Mn}^{3+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$, respectively (denoted as $0.6\text{Cu}0.3\text{Mn}/\text{Al}$, same below) [43]. For the $0.6\text{Cu}0.3\text{Mn}/\text{Al}$ sample, after a CO pretreatment at 325°C , the catalytic activity and selectivity for NO+CO reaction are improved obviously, and significantly higher than those of the samples of $\gamma\text{-Al}_2\text{O}_3$ -supported single oxides of CuO or Mn_2O_3 (Fig. 14). UV-Visible diffuse reflection spectra (UV-Vis DRS) characterization result of $0.3\text{Mn}/\text{Al}$ sample exhibits the absorption peak of octahedral Mn species at 270 nm , indicating that the dispersed Mn^{3+} species occupy octahedral vacancies on the surface of $\gamma\text{-Al}_2\text{O}_3$ [43]. From Incorporation Model, when the dispersed copper ions and manganese ions occupy the octahedral vacancies of $\gamma\text{-Al}_2\text{O}_3$, three kinds of $\text{Cu}^{2+}\text{-O-Cu}^{2+}$, $\text{Cu}^{2+}\text{-O-Mn}^{3+}$, and $\text{Mn}^{3+}\text{-O-Mn}^{3+}$ species are formed on the surface of $\gamma\text{-Al}_2\text{O}_3$ (Fig. 15(a–c)). XPS and Electron paramagnetic resonance (EPR) results show that the surface Cu^{2+} and Mn^{3+} are reduced to Cu^+ and Mn^{2+} species after

CO pretreatment, which indicates that CO pretreatment will take away the oxygen species between the surface dispersed components to form $\text{Cu}^+\text{-}\square\text{-Cu}^+$, $\text{Cu}^+\text{-}\square\text{-Mn}^{2+}$, and $\text{Mn}^{2+}\text{-}\square\text{-Mn}^{2+}$ structures (Fig. 15(a'–c')) [43]. We define the generated oxygen vacancy between the different Cu^+ and Mn^{2+} ions as SSOV. By comparing the catalytic performance of $0.6\text{Cu}/\text{Al}$, $0.3\text{Mn}/\text{Al}$, and $0.6\text{Cu}0.3\text{Mn}/\text{Al}$ samples before and after CO pretreatment for NO+CO reaction, it can be seen that SSOV plays a very important role in improving the catalytic performance for NO+CO reaction.

In order to approach the catalytic mechanism of SSOV in NO+CO reaction, a variety of in situ characterizations have been carried out on CuMn/Al catalyst before and after CO pretreatment [43]. In situ Fourier transform infrared (In situ FT-IR) competitive adsorption results confirm that CO adsorbed on Cu^+ and NO adsorbed on Mn^{2+} . NO-temperature program desorption (NO-TPD) experiments further show that the emergence of SSOV favors to promote the dissociation of NO. Based on Incorporation Model and the in situ FT-IR results of NO and

Fig. 14. Catalytic performance of $0.6\text{Cu}/\text{Al}$, $0.3\text{Mn}/\text{Al}$, and $0.6\text{Cu}0.3\text{Mn}/\text{Al}$ samples before and after CO pretreatment for the NO+CO reaction [43].

Fig. 15. Schematic diagram of the surface structure of CuO and Mn_2O_3 supported on the (110) plane of $\gamma\text{-Al}_2\text{O}_3$ (C-Layer) before and after CO pretreatment. (a) $0.6\text{Cu}/\text{Al}$; (b) $0.6\text{Cu}0.3\text{Mn}/\text{Al}$; (c) $0.3\text{Mn}/\text{Al}$; (a') $0.6\text{Cu}/\text{Al-CO}$; (b') $0.6\text{Cu}0.3\text{Mn}/\text{Al-CO}$; (c') $0.3\text{Mn}/\text{Al-CO}$ [43].

Fig. 16. Reaction mechanism for NO reduction by CO over CuMn/Al samples after CO pretreatment [43].

CO adsorption and the catalytic performance results, the NO+CO reaction mechanism involving SSOV and SOV in CuO-Mn₂O₃/γ-Al₂O₃ catalyst is proposed (Fig. 16). When 0.6Cu0.3Mn/Al catalyst is pretreated by CO, O²⁻ between copper and manganese or between manganese and manganese can be removed, which generates SSOV and SOV (step ①). When NO and CO gases are introduced into the reactor, NO adsorbed on Mn²⁺ and CO adsorbed on Cu⁺ (step ②). The existence of SSOV between Mn²⁺ and Cu⁺ provides the nearest vacancy for NO dissociation, so NO dissociates into N radical and O radical. Furthermore, the formation of CO₂ by O radical reacting with the neighboring CO adsorbed on Cu⁺ (2144 cm⁻¹) is observed

(step ③). The -NCO species is generated by N radical reacting with CO molecule in the gas phase (2214 cm⁻¹, step ④), and then the -NCO species reacts with the neighbor NO molecule adsorbed on Mn²⁺ through SOV to generate CO and N₂O (step ⑤). The generated N₂O is adsorbed again on Mn²⁺ (2241 cm⁻¹, step ⑥) and further reduced by CO adsorbed on the neighbor Cu⁺ to form CO₂ and N₂ (step ⑦). Finally, the SSOV active site is regenerated to promote the catalytic reaction process cyclically. Through the above discussion of the catalytic mechanism, we recognize that the exposed Cu⁺ and Mn²⁺ are the adsorption sites for CO and NO, respectively, and SSOV plays a key bridge role between steps ② and ③, which make the whole surface reaction proceed smoothly. Therefore, the synergistic effect of SSOV and SOV plays a key role in promoting the catalytic performance of CuO-Mn₂O₃/γ-Al₂O₃ catalyst after the CO pretreatment for NO+CO reaction.

Based on the investigation above, it is recognized that SOV plays an important role in the catalytic reaction. Especially for the complex supported dual metal oxide catalysts, the generation of SSOV can enhance the catalytic performance for NO elimination remarkably. To verify the universality of SSOV, CuO-CoO/γ-Al₂O₃ model catalysts are prepared by co-impregnation method to investigate the effect of CO pretreatment on the catalytic performance [44]. In the third section, it has been confirmed that Cu²⁺-O-Co²⁺ species can exist in CuO-CoO/γ-Al₂O₃ catalysts. Moreover, the capping oxygen can be removed to form Cu⁺-□-Co²⁺ species in the process of CO pretreatment (□ is SSOV). From the results of NO+CO reaction, it is known that the catalytic performance of CuO-CoO/γ-Al₂O₃ catalysts is improved dramatically after CO pretreatment due to the formation of SSOV (Fig. 17). The obtained results suggest

Fig. 17. NO conversion and N₂ selectivity over 0.6Cu_yCo/Al catalysts with different cobalt oxide loadings before and after CO pretreatment. The reaction temperatures are shown in the figures.

that SSOV has a certain degree of universality. Recently, we find that the catalytic performance of NiO-Mn₂O₃/γ-Al₂O₃ catalysts for NO+CO reaction is also improved significantly after CO pre-treatment. Of course, for the systems of the supported dual metal oxide catalysts on other supports (such as TiO₂, etc.) or catalysts without CuO, whether SSOV can be used to explain their catalytic performance and whether SSOV has a wider range of applications need further study.

5. Summary and outlook

With γ-Al₂O₃ as the support, the dispersed states of a supported single metal oxide (CuO) and dual metal oxides (CuO-Mn₂O₃, CuO-CoO) are investigated systematically. Based on the consideration of Incorporation Model, the surface dispersion behaviors and physicochemical properties of CuO by itself and when it is modified by another metal oxide on the surface of γ-Al₂O₃ have been explained. Through a variety of characterization methods (including some in situ and quasi situ methods), combined with the catalytic performance in CO+O₂ and NO+CO model reactions, we established the structure-activity relationships of the catalysts in the reactions, and proposed a reaction mechanism involving SSOV. However, the continuing study of Incorporation Model will meet much difficulty due to the complexity of composition and structure of the supported metal oxide catalysts as well as the restriction of experimental techniques. In the future, metal oxide nanocrystals with regular morphology and exposed specific crystal plane will be prepared as supports to simplify the catalyst systems, moreover, combining with theoretical chemistry method (quantum chemistry) to carry out further research on Incorporation Model. Meanwhile, the investigation of the universality of SSOV and the related properties research in catalytic reactions will be continued.

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Graphical Abstract

Chin. J. Catal., 2013, 34: 1975–1985 doi: 10.1016/S1872-2067(12)60708-6

The application of incorporation model in γ-Al₂O₃-supported single and dual metal oxide catalysts: A review

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This review summarizes the research progress of the Incorporation Model in γ-Al₂O₃-supported single and dual metal oxide catalysts for CO+O₂ and NO+CO model reactions and proposes a reaction mechanism involving SSOV.

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“嵌入模型”在 γ - Al_2O_3 负载单组分和双组分金属氧化物催化剂中的应用

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摘要: 探讨负载型金属氧化物催化剂的表面组分与载体之间的相互作用, 有助于理解相关催化剂的催化作用本质. 近年来, 我们对单组分CuO以及双组分CuO-Mn₂O₃, CuO-CoO等金属氧化物在 γ -Al₂O₃载体表面的分散行为和存在状态, 及其物理化学性质和催化性能(CO+O₂和NO+CO模型反应)进行了研究. 结果表明, 这些金属氧化物在 γ -Al₂O₃载体表面的分散行为和所得负载型催化剂样品的一些物理化学性质及其催化性能均可参照“嵌入模型”来解释. 在此基础上, 我们讨论了这些样品的“组成-结构-性质”间的关系, 并针对表面负载双组分金属氧化物样品提出了表面协同氧空位参与的NO+CO反应机理.

关键词: γ -氧化铝载体; 负载型金属氧化物催化剂; 表面相互作用; 嵌入模型; 表面协同氧空位

收稿日期: 2013-08-31. 接受日期: 2013-09-10. 出版日期: 2013-11-20.

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基金来源: 国家自然科学基金(20873060, 20973091); 国家重点基础研究发展计划(973计划, 2010CB732300); 江苏省科技支撑计划工业项目(SBE201100389).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).