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Article

Influence of calcination and pretreatment conditions on the activity of Co_3O_4 for CO oxidation

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ABSTRACT

The influence of calcination and pretreatment conditions on the structure of Co_3O_4 and its activity for CO oxidation were studied. TG analysis indicated that the precursor of Co_3O_4 prepared by a precipitation method was present in the form of cobalt hydroxide carbonate, calcination of which within the temperature range of 150–400 °C in air resulted in the formation of cubic phase Co_3O_4 . N_2 adsorption-desorption, powder X-ray diffraction, transmission electron microscopy, and activity test results showed that the prepared Co_3O_4 samples were comprised of nanoparticles, with the specific surface area and size distribution closely related to the calcination temperature. Over these samples, a size dependence of the catalytic activity for CO oxidation was clearly observed. As identified by positron annihilation lifetime spectrum, low temperature oxygen temperature-programmed desorption, and durability testing for CO oxidation, pretreatment of Co_3O_4 in N_2 within the temperature range 150–250 °C favors the formation of surface oxygen vacancy clusters, the occurrence of which would be beneficial for the adsorption and activation of O_2 , and also for the catalytic oxidation of CO. Meanwhile, the reconstruction of oxygen vacancies on the surface of Co_3O_4 , induced by the pretreatment process, was also discussed.

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1. Introduction

Tricobalt tetraoxide (Co_3O_4) has been attracting much attention in heterogeneous catalysis due to its excellent performance in the catalytic oxidation of CO and hydrocarbons [1,2]. Typically, Co_3O_4 has a spinel structure which consists of Co^{3+} cations in octahedral sites and Co^{2+} cations in tetrahedral sites. In this structure, accordingly, there are two kinds of oxygen ion: one is bonded to three Co^{3+} ions, while another is bonded to one Co^{3+} and one Co^{2+} ion as the nearest neighbors [3,4]. It has been demonstrated that the catalytic activity of Co_3O_4 for CO oxidation is closely related to the ratio of $\text{Co}^{3+}/\text{Co}^{2+}$ on the predominantly exposed planes, and the adsorption and activa-

tion of molecular oxygen [1]. With this in mind, there are two strategies to design and synthesize Co_3O_4 with high catalytic performance. Firstly, precise tuning of $\text{Co}^{3+}/\text{Co}^{2+}$ on the surface of Co_3O_4 was successfully realized using controlled synthesis of nano materials, thus creating desired catalysts with excellent activity. By using a hydrothermal method, recently, Co_3O_4 nanorods preferentially exposing the reactive (110) planes were prepared by Xie et al. [5], on which Co^{3+} cations are solely present. This feature of Co_3O_4 nanorods is favorable for the adsorption of CO and its further reaction with neighboring oxygen to produce CO_2 , and finally resulting in complete oxidation of 1% CO even at temperatures as low as –77 °C. Similarly, Hu et al. [6] prepared Co_3O_4 nanobelts and nanocubes by a hydro-

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thermal method. The former had predominant exposure of (011) planes while the latter had a predominance of exposed (001) planes. Such features provide Co^{3+} sites with different activities for CO oxidation. By using KIT-6 as hard template, Ren et al. [7] created crystalline mesoporous Co_3O_4 , on which completely oxidation of 1% CO was realized at the temperature of $-50\text{ }^\circ\text{C}$ after pretreatment in 8% O_2 at $400\text{ }^\circ\text{C}$. Considering the crucial roles of oxygen vacancies in the activation of oxygen and the catalytic oxidation of CO over Co_3O_4 [8,9], on the other hand, substitution of Co with hetero-atoms or pretreatment under suitable conditions has been employed to create cobalt oxide-based catalysts with high efficiency. Cerium-substituted Co_3O_4 catalysts were prepared by Luo et al. [10], among which a sample with $\text{Co}/(\text{Co} + \text{Ce})$ atomic ratio of 0.3 gave the largest amount of oxygen vacancies, and exhibited the highest activity for low temperature CO oxidation. Lou et al. [11] also found that doping of Co_3O_4 with Bi_2O_3 promoted the formation of oxygen vacancies, accelerating the adsorption and activation of oxygen, thus enhancing its performance in CO oxidation. Indeed, 20% Bi_2O_3 - Co_3O_4 could completely oxidize CO (1%) even at a temperature of $-89\text{ }^\circ\text{C}$. Over this catalyst, meanwhile, complete CO conversion was maintained at $-75\text{ }^\circ\text{C}$ for 600 min. By using $\text{Co}(\text{NO}_3)_2$ as a precursor of cobalt and $(\text{NH}_4)_2\text{CO}_3$ serving as a precipitant, Co_3O_4 catalysts were prepared by Wang et al. [12]. Over these samples, the O_2^- and O^- species were responsible for low temperature CO oxidation, which was confirmed by activity testing and oxygen temperature-programmed desorption (O_2 -TPD) analysis. As suggested by Sadykov and co-workers [9], the surface reconstruction of Co_3O_4 induced by He pretreatment at $350\text{ }^\circ\text{C}$ was favorable for the formation of oxygen species weakly bound on the surface, and thus enhanced CO oxidation at low temperatures. More recently, Yu et al. [13] found that pretreatment of Co_3O_4 in an atmosphere of air, or nitrogen, or CO/air promoted the formation of surface oxygen vacancies, on which the adsorption and activation of molecular oxygen were triggered. This feature induced by pretreatment was beneficial for low temperature CO oxidation over Co_3O_4 , enabling complete oxidation of 1% CO at $-80\text{ }^\circ\text{C}$.

In order to optimize the conditions employed for Co_3O_4 preparation, herein, the influence of calcination temperature on the activity of Co_3O_4 for CO oxidation was intensively studied. Meanwhile, positron annihilation lifetime spectrum (PALS) and O_2 -TPD analyses were carried out to identify the impacts of pretreatment conditions on the formation of surface oxygen vacancies and on the adsorption and activation of oxygen.

2. Experimental

2.1. Co_3O_4 preparation

Co_3O_4 was prepared by a precipitation method as reported in previous studies [13,14]. Typically, an aqueous solution of Na_2CO_3 with a concentration of 0.15 mol/L was heated to $70\text{ }^\circ\text{C}$ and quickly poured into an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (0.12 mol/L, also heated at $70\text{ }^\circ\text{C}$), followed by further aging at 60 – $70\text{ }^\circ\text{C}$ for 1 h under vigorous stirring. After cooling down to room temperature and standing for another 2 h, the precipitate was

repeatedly washed with distilled water (heated below $70\text{ }^\circ\text{C}$) and centrifugally separated, until the pH value of the solution was ~ 8.0 . The solid obtained was dried at $100\text{ }^\circ\text{C}$ overnight and calcined in air within the temperature range of 120 – $400\text{ }^\circ\text{C}$ for 4 h. Before measurement, the sample was crushed and sieved to ensure particles were between 60–90 mesh in size.

2.2. Activity test

The catalytic tests for CO oxidation were carried out in a fixed-bed quartz reactor (i.d. = 5 mm), containing 150 mg of catalyst samples. A standard reaction gas containing 1.0 vol% CO, 20 vol% O_2 , and 0.018 vol% H_2O was fed at a total flow rate of 50 ml/min (GHSV = 20000 ml/(h·g)). In all cases, pretreatments were performed at the desired temperatures (120 – $250\text{ }^\circ\text{C}$) for 40 min in a stream of N_2 or dry air at a flow rate of 50 ml/min. The concentrations of CO in the inlet and outlet streams were measured by using an automatic sampling gas chromatograph (GC8A, Shimadzu Corporation), and then the conversion of CO was calculated based on the changes of CO concentrations. The temperature was typically lowered from room temperature using a methanol/liquid nitrogen mixture contained in a vacuum bottle.

2.3. Co_3O_4 characterization

BET surface areas were determined by nitrogen adsorption at $-196\text{ }^\circ\text{C}$ by using a Quantachrome Autosorb (IQ) instrument. Prior to N_2 physisorption, the catalysts were degassed at $120\text{ }^\circ\text{C}$ for 4 h. Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a X'Pert PRO MPD instrument using $\text{Cu K}\alpha$ radiation. The patterns were measured over the 2θ range from 10° to 90° at a scan step of 0.02° . Thermal gravity (TG) analysis of an uncalcined sample was performed on a TGA-50 analyzer (Shimadzu Corporation). The morphology and the particle size distribution of the prepared samples were examined by a Hitachi H-7500 transmission electron microscope (TEM) with 80 kV acceleration voltage.

O_2 -TPD experiments were performed at Automated Catalyst Characterization System (Autochem 2920, Micromeritics, USA) equipped with a mass spectrometer (QIC 20, Hiden, UK) by using 200 mg catalyst powder [13]. After pretreatments at different conditions, the sample was cooled down to $-70\text{ }^\circ\text{C}$, and then exposed to O_2 at the same temperature. After 60 min, the feed gas was switched to He for purging the system for 60 min and then the temperature was raised at a ramp of $10\text{ }^\circ\text{C}/\text{min}$ from -70 to $600\text{ }^\circ\text{C}$ in a stream of He at 30 ml/min. During this process, the mass signal of O_2 ($m/z = 32$) was recorded.

PALS measurements were carried out on a positron annihilation lifetime spectrometer at the Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, CAS. It consists of a BaF_2 scintillation crystal detector coupled with nuclear electronic plug-in components and a fast-slow coincidence system, with a time resolution of 190 ps full-width at half-maximum (FWHM). During the measurement, two pieces of the same Co_3O_4 samples were set in front of and behind the ^{22}Na source, respectively, which was also located at the axial

center of two detectors. After pretreatment under different conditions, the samples together with the ^{22}Na source were sealed in a rubber balloon filled with nitrogen, to avoid surface changes such as oxygen vacancy changes induced by the adsorption of water vapor during the measurement. The positron annihilation results were fitted with LT9.0 software.

3. Results and discussion

3.1. Analysis of the precursor of Co_3O_4

Figure 1 shows the TG and DTG profiles of the precursor of Co_3O_4 which had been dried at 100 °C overnight. Within the temperature range of 100–620 °C, a mass loss of 24.6% was observed during this measurement. Generally, the uncalcined sample, which was prepared using Co^{2+} as cobalt precursor and carbonate as precipitant, was present as cobaltous dihydroxycarbonate ($\text{Co}_2(\text{OH})_2\text{CO}_3$) [15,16]. During the transformation of this precursor to the Co_3O_4 structure, a mass loss of 24.2% should occur, which is in good agreement with our experimental result. This result clearly suggests that the uncalcined sample mainly consists of $\text{Co}_2(\text{OH})_2\text{CO}_3$. Based on the result exhibited in Fig. 1, meanwhile, it can be seen that stable catalysts could be created by calcination at temperatures above 250 °C.

3.2. Influence of calcination temperature on the structure and catalytic performance of Co_3O_4

XRD patterns of samples calcined within the temperature range of 120–400 °C are shown in Fig. 2. During calcination at 120 °C, hydroxyl and carbonate groups contained in $\text{Co}_2(\text{OH})_2\text{CO}_3$ were decomposed and partially removed, resulting in the formation of cubic phase Co_3O_4 (JCPDS 42-1467). Over the sample calcined at 120 °C, meanwhile, reflection peaks that can be indexed to $\text{Co}_2(\text{OH})_2\text{CO}_3$ were observed [16]. As for the sample calcined at 150 °C, only the characteristic peaks due to Co_3O_4 were observed. Further increasing the calcination temperature resulted in a gradually increased intensity of Co_3O_4 peaks, indicating a higher crystallinity and in agreement with the result of Wang et al. [12,17]. By using the Scherrer equation, the particle sizes of samples

Fig. 1. TG and DTG profiles of the precursor of Co_3O_4 prepared by precipitation method.

Fig. 2. XRD patterns of as prepared Co_3O_4 samples calcined in air at different temperatures.

calcined at different temperatures were calculated from the peaks indexed to Co_3O_4 , with the results listed in Table 1. Table 1 also shows the BET surface areas of the samples described above. Generally, the higher the temperature employed in the calcination process, the lower the surface area and the larger the particle size. Particularly for the samples calcined at temperatures above 350 °C, this tendency was more pronounced, which may significantly change the activity for CO oxidation [1]. It should be noted that the sample calcined at 120 °C exhibited the highest surface area, while giving the largest particle size as calculated by the Scherrer equation. Possibly, a relatively large error is introduced if the particle size is calculated on the assumption that the entire sample could be indexed to the Co_3O_4 structure. For this sample, indeed, reflection peaks assignable to Co_3O_4 and $\text{Co}_2(\text{OH})_2\text{CO}_3$ were both seen in the XRD patterns.

TEM characterization was also performed on the samples calcined at different temperatures, with typical images shown in Fig. 3. The Co_3O_4 nanoparticles exhibited irregular shapes with uniform size. A similar size distribution was observed for the samples calcined within the temperature range of 200–300 °C, while an obvious increase in diameter was confirmed for the samples calcined at 400 °C, which was in agreement with the

Table 1

BET surface area, particle size, and T_{50} for CO oxidation over Co_3O_4 samples calcined in air at different temperatures.

Calcination temperature (°C)	BET surface area ^a (m ² /g)	Particle size ^b (nm)	T_{50} ^c /°C
120	187.8	20.3	91
150	141.6	9.4	–108
200	136.1	10.7	–112
250	132.9	11.8	–113
300	129.4	13.3	–118
350	71.4	15.1	–89
400	47.5	19.9	–56

^a Before the measurement, the sample was pretreated at 120 °C for 4 h.

^b Calculated using the Scherrer equation over the peak due to (311) plane.

^c Temperature required for 50% CO conversion after pretreated by N_2 at 150 °C for 40 min (except that Co_3O_4 calcined at 120 °C was pretreated at 120 °C).

Fig. 3. TEM images of Co_3O_4 calcined at 200 °C (a), 300 °C (b), and 400 °C (c).

results of XRD.

Figure 4 shows the activity of samples calcined at different temperatures for CO oxidation. As mentioned above, the pretreatment atmosphere and temperature significantly changed the activity of Co_3O_4 for CO oxidation [13]. To avoid such an influence, all the samples were pretreated in N_2 for 40 min at 150 °C except that the sample calcined at 120 °C was also pretreated at 120 °C (to avoid the influence of pretreatment at high temperatures on the structure and catalytic performance). The sample calcined at 120 °C could completely oxidize 1% CO at temperatures above 100 °C. However, the samples calcined within the temperature range of 200–300 °C gave higher activity for CO oxidation, exhibiting 100% CO conversion even at temperatures as low as –80 °C. Clearly, further increasing the calcination temperature decreases the activity of Co_3O_4 for CO oxidation.

Figure 5 further shows the relationship between BET surface area and T_{50} for CO oxidation on Co_3O_4 samples calcined at different temperatures. Samples calcined within the temperature range of 150–300 °C possessed similar specific surface area, and thus showed no significant difference in T_{50} for CO

Fig. 4. Influence of calcination temperature on performance of Co_3O_4 for CO oxidation. Before the measurement, the catalyst was pretreated by N_2 for 40 min at 150 °C except that the sample calcined at 120 °C was also pretreated at 120 °C. Reaction conditions: 1% CO/air, 50 ml/min, catalyst 150 mg, SV = 20000 ml/(h·g).

oxidation. Calcination of the samples above 300 °C sharply decreased their surface area, which was finally related to a significant increase in the values of T_{50} . Over the samples calcined at 150–400 °C, there is a close relationship between the surface areas and the activity for CO oxidation, which is in agreement with the results of Wang et al. [12,17].

3.3. Influence of pretreatment conditions on the formation of oxygen vacancies and catalytic performance of Co_3O_4 for low temperature CO oxidation

As a powerful technique, recently, PALS characterization has been successfully used in the measurement of atomic vacancies located on solid materials [18,19]. Particularly, insights on heterogeneous catalysts have been achieved in revealing active sites such as oxygen vacancies [20–22]. With this in mind, herein, PALS measurement was also employed to identify the change of oxygen vacancies on the Co_3O_4 surface induced by pretreatment. At a microscopic level, revealing this change may provide an opportunity for understanding the influence of pretreatment on the catalytic performance of Co_3O_4 for CO oxidation.

As shown in Table 2, the PALS spectra of all the samples exhibited three distinct lifetime values, τ_1 , τ_2 , and τ_3 , indicating three kinds of vacancies with different sizes present on the surface of Co_3O_4 [21]. The longest value of τ_3 (2.08–3.27 ns), the

Fig. 5. Relationship between BET surface area and T_{50} for CO oxidation on Co_3O_4 samples calcined at different temperatures.

Table 2

PALS analysis of Co_3O_4 calcined at 300 °C after pretreatment in different atmospheres and at different temperatures.

Sample	τ_1^a/ps	τ_2^a/ps	τ_3^a/ns	$I_1^b/\%$	$I_2^b/\%$	$I_3^b/\%$
Non-pretreatment	217	384	2.94	57.1	40.9	2.0
Air pretreatment at 150 °C	223	420	3.27	59.1	39.1	1.8
N_2 pretreatment at 150 °C	194	361	2.14	38.7	59.9	1.3
N_2 pretreatment at 200 °C	204	377	2.29	36.0	63.3	0.7
N_2 pretreatment at 250 °C	190	375	2.08	27.7	71.2	1.1

^a Lifetime of positrons annihilated at different vacancies.

^b Relative intensities of different vacancies.

so-called bulk lifetime, was assigned to the annihilation of positrons in the large voids present in the sample. The shortest one (τ_1), with the value of 190–223 ps, was due to a small oxygen vacancy, probably in the form of $\text{Co}^{2+}-\square-\text{Co}^{2+}$ (hereafter, denoted as single oxygen vacancy), the formation of which may originate from the removal of twofold-coordinate oxygen ($\text{Co}^{2+}-\text{O}-\text{Co}^{3+}$) on the Co_3O_4 surface [4,23]. The intermediate one (τ_2 , 361–420 ps) could be assigned to surface oxygen vacancy clusters (denoted as VCs hereafter), such as dimers, trimers, or larger vacancies.

The relative intensities of different vacancies described above are also presented in Table 2, denoted as I_1 , I_2 , and I_3 , corresponding to single oxygen vacancies (τ_1), VCs (τ_2), and large voids (τ_3), respectively. By comparison with the sample calcined at 300 °C in air, it is easily found that pretreatment hardly changes the size of large voids and their intensity, while the situation is quite different for the single oxygen vacancies and vacancy clusters. After pretreatment in air at 150 °C, the value of τ_2 increased to some degree, while hardly changing its intensity. It is interesting to note that pretreatment in N_2 at the same temperature of 150 °C significantly increased the value of I_2 at the expense of an obvious decrease in I_1 , while this process had a marginal effect on the size of VCs (τ_2). Further increase in pretreatment temperature gradually increased the value of I_2 , which was also accompanied by a decrease of I_1 . After pretreating the sample at 250 °C in N_2 , indeed, the value of I_2 rose to 71.2%. This result strongly suggests that pretreatment in N_2 at suitable temperatures significantly increases the relative concentration of VCs on the Co_3O_4 surface, at the expense of a decrease in the amount of single oxygen vacancies.

As for CO oxidation over Co_3O_4 nanorods, Xie et al. [5] proposed that the surface Co^{3+} cations on Co_3O_4 play crucial roles in the adsorption of CO and its further interaction with neighboring oxygen to produce CO_2 . The abstraction of neighboring oxygen results in the formation of a surface oxygen vacancy, replenishment of which can be achieved by a gas-phase oxygen molecule, and thus the Co^{3+} active sites are regenerated. On the other hand, Yu et al. [13] suggested that oxygen vacancies present on the surface of Co_3O_4 nanoparticles are responsible for the activation of molecular oxygen, thus contributing to CO oxidation. To verify which of the two proposed mechanisms is dominant for CO oxidation on the $\text{Co}_3\text{O}_4(110)$ surface, an elegant density functional theory plus on-site Coulomb repulsion (DFT + U) calculation was performed by Jiang and Dai [23]. It was found that hopping of a twofold-coordinate oxygen to a neighboring single oxygen vacancy has a barrier of only 0.26

eV, indicating a high mobility of single oxygen vacancies and thus leading to the formation of VCs (such as dimers). Meanwhile, it was proposed that the desorption of two oxygen atoms both located at twofold-coordinate sites to form an O_2 molecule costs a lot of energy (~ 5 eV), probably beyond that available at the moderate pretreatment temperatures of 150–250 °C (used by Yu et al. [13]). In other words, the energy provided by such pretreatment may be not sufficient for the formation of VCs on Co_3O_4 surface. However, it should be pointed out that this deduction based on DFT + U calculation was proposed without considering the following aspects. Firstly, the presence of single oxygen vacancies on the calcined Co_3O_4 , which was identified by PALS measurement, was neglected. With this in mind, the possibility of VCs formation derived from the transformation of single oxygen vacancies and their further aggregation was not taken into account during the pretreatment of the sample in suitable atmospheres such as in N_2 . Secondly, extraction of a surface oxygen atom from a site neighboring a single oxygen vacancy also creates VCs, for which the reaction energy barrier should be much lower than that of the desorption of two neighboring oxygen atoms [24], and this possibility should also be taken into account. Based on these aspects, it is possible that pretreatment in N_2 at appropriate temperatures induces transformation of single oxygen vacancies and their further aggregation, the occurrence of which results in the formation of VCs. The increase in the concentration of VCs may also be derived from extraction of a surface oxygen atom from a site nearby a single oxygen vacancy, the pathway of which can be described as shown in Scheme 1.

Mitsui et al. [25] reported that even for the simple reaction of H_2 dissociation on the model catalyst Pd(111), aggregates of three or more hydrogen vacancies are required, indicating the crucial role of VCs in catalytic reactions. Similarly, the calculated result provided by Jiang et al. [22] also proposed that two neighboring single oxygen vacancies working together is more efficient for O_2 activation than those working alone, and thus VCs (such as divacancies) contribute to CO oxidation on the $\text{Co}_3\text{O}_4(110)$ surface. With these in mind, Fig. 6 presents a relationship between the relative amount of adsorbed molecular oxygen (Ad-O_2) and the relative concentration of VCs (I_2) on Co_3O_4 with different pretreatments. The values of Ad-O_2 over Co_3O_4 samples after different pretreatments have been measured by low temperature O_2 -TPD, and detailed information can

Scheme 1. Proposed restructuring mechanism of oxygen vacancies on the surface of Co_3O_4 during N_2 pretreatment.

Fig. 6. Relationship between the relative amount of adsorbed molecular oxygen (Ad-O₂) and the relative concentration of oxygen vacancy clusters (I₂) on the surface of Co₃O₄ samples with different pretreatments.

be found in our previous paper [13]. Clearly, a higher concentration of VCs results in a larger amount of adsorbed O₂ on Co₃O₄. In particular, an excellent linear relationship was observed between the amount of adsorbed O₂ and the value of I₂ for the samples pretreated in N₂ at different temperatures, strongly suggesting the key roles of VCs in the adsorption and activation of O₂.

It was proposed that the catalytic oxidation of CO at low temperatures follows a pathway involving reactive molecular oxygen [26]. This prompts us to consider that a change of surface oxygen vacancies induced by pretreatment should impact the catalytic performance of Co₃O₄ for CO oxidation because the VCs can serve as effective traps for O₂. Figure 7 shows the activity of Co₃O₄ with different pretreatments for CO oxidation at 0 °C. After pretreatment in air at 150 °C, complete oxidation of 1% CO was maintained at 0 °C for 37 h, which was followed by a gradual decrease in CO conversion with time on stream. This result possibly suggests that the active sites such as oxygen vacancies were poisoned by carbonates produced during the oxidation of CO [23]. Meanwhile, it should be noted that the activity of Co₃O₄ for CO oxidation was usually deactivated by the presence of moisture, even by a trace amount of water vapor co-existing in the feed gas [13,14]. Consequently, the activity loss may also be due to the adsorption of water vapor on oxygen vacancies. Over the sample pretreated in N₂ at the same temperature of 150 °C, interestingly, 100% CO conversion was maintained at 0 °C for 69 h. Increasing the pretreatment temperature to 200 °C resulted in a longer durability for CO oxidation, exhibiting a value of 91 h for 100% CO conversion at 0 °C.

Furthermore, Fig. 8 presents a relationship between the value of Ad-O₂ and the durability of Co₃O₄ samples with different pretreatments for CO oxidation. Clearly, the larger the amount of Ad-O₂ on Co₃O₄, the longer the durability for CO oxidation is. This result possibly suggests that the VCs on the Co₃O₄ surface not only contributed to the activation of O₂, but were also available for the adsorption of carbonate and water molecules. A higher concentration of VCs indicates a larger capacity for carbonate and water molecule adsorption, thus retarding their negative effects on the activation of O₂, and finally guaranteeing a longer durability for the catalytic oxida-

Fig. 7. Influence of pretreatment conditions on the durability of Co₃O₄ for CO oxidation at 0 °C. Before the measurement, the catalyst was pretreated by N₂ or air for 40 min at different temperatures. Reaction conditions: 1% CO/air 50 ml/min, catalyst 150 mg, SV = 20000 ml/(h·g). The inset is O₂-TPD profiles of fresh and used Co₃O₄ samples after pretreatment in N₂ for 40 min at 150 °C. The first run was operated within the temperature range of -70–20 °C.

tion of CO. These results further confirm the key role of VCs on the low temperature CO oxidation over Co₃O₄ by serving as traps for O₂ adsorption and its further activation.

Meanwhile, the deactivated Co₃O₄ was further treated by the same manner of pretreatment employed in the study described above, and then its activity was evaluated for CO oxidation. As shown in Fig. 7, after pretreating the deactivated sample in N₂ at 150 °C again, its activity for CO oxidation at 0 °C was fully recovered. In this case, it is likely that the adsorbed carbonate and water molecules will be removed from the surface of Co₃O₄, resulting in replenishment of VCs which are thus available again for the activation of O₂ and the catalytic oxidation of CO. This assumption was further verified by the O₂-TPD result (the inset of Fig. 7), in which the capacity of deactivated Co₃O₄ for O₂ adsorption was recover by the second pretreatment. This result also confirms a recoverability of Co₃O₄ for CO oxidation via pretreatment under suitable conditions.

Fig. 8. Relationship between the relative amount of molecular oxygen adsorbed on the surface of Co₃O₄ samples with different pretreatments and their durability for CO oxidation.

Graphical Abstract

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Influence of Calcination and Pretreatment Conditions on the Activity of Co_3O_4 for CO Oxidation

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Pretreatment of Co_3O_4 in N_2 at moderate temperatures promotes the formation of oxygen vacancy clusters, favoring the adsorption of oxygen molecules and guaranteeing a long durability for CO oxidation.

4. Conclusions

Low temperature CO oxidation over Co_3O_4 is sensitive both to the particle size of samples and the number of surface oxygen vacancies. The particle size and specific surface area of Co_3O_4 prepared by the precipitation method are closely related to the calcination temperature. Calcining the sample within the temperature range of 150–300 °C creates Co_3O_4 with high surface area and small particle size, exhibiting high catalytic activity for CO oxidation at low temperatures. The durability of Co_3O_4 for CO oxidation is positively correlated to the relative concentration of surface oxygen vacancy clusters. Pretreatment of the sample in N_2 at suitable temperatures (150–250 °C) promotes the formation of VCs, the presence of which favors the adsorption and activation of oxygen molecules, guaranteeing a long durability for CO oxidation. Meanwhile, pretreatment of deactivated samples replenished the ability of Co_3O_4 for O_2 adsorption. As a result, the catalytic performance of Co_3O_4 for CO oxidation was regenerated, further confirming the essential role of VCs in low temperature CO oxidation.

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焙烧与预处理条件对 Co_3O_4 催化氧化 CO 性能的影响

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摘要: 采用沉淀法制备了 Co_3O_4 , 考察了焙烧和预处理条件对其结构、低温催化氧化 CO 性能的影响. 热重分析表明, 未经焙烧的样品以 $\text{Co}(\text{OH})_2\text{CO}_3$ 的形式存在, 150~400 °C 空气气氛中焙烧后, 样品以立方相 Co_3O_4 的形式存在. N_2 吸附-脱附法、X 射线衍射、透射电镜及活性测试结果表明, 以纳米颗粒物存在的 Co_3O_4 的比表面积、颗粒尺寸、催化氧化 CO 活性与焙烧温度密切相关. 正电子湮没寿命谱、 O_2 -程序升温脱附与定温条件下 CO 氧化测试结果表明, 合适温度 (150~250 °C) 下 N_2 预处理有利于 Co_3O_4 表面氧空穴的形成, 它在吸附活化分子氧以及 CO 催化氧化反应中起到关键作用. 同时讨论了预处理作用下 Co_3O_4 表面氧空穴的再构机制.

关键词: 四氧化三钴; 焙烧; 预处理; 氧空穴; 一氧化碳氧化

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1. 前言

Co_3O_4 因具有优异的催化氧化 CO 及碳氢化合物性能而广受关注^[1,2]. Co_3O_4 是一种典型的尖晶石结构, 其中 Co 以八面体配位的 Co^{3+} 和四面体配位的 Co^{2+} 存在. 与此对应, O 也有两种存在形态: 三配位 O, 即同时与三个 Co^{3+} 相连; 和两配位 O, 即同时与一个 Co^{3+} 和一个 Co^{2+} 结合^[3,4]. 研究表明^[1], Co_3O_4 上 CO 氧化反应性能与 $\text{Co}^{3+}/\text{Co}^{2+}$ 、氧的吸附与活化密切相关, 关注以上性能的调控衍生出两种设计与制备高性能 Co_3O_4 策略. 一方面, 人们利用纳米材料可控合成技术, 实现了 Co_3O_4 上 $\text{Co}^{3+}/\text{Co}^{2+}$ 的精确调控, 合成了性能优异的催化剂. Xie 等^[5]以水热法合成了 Co_3O_4 纳米棒, 其主要暴露晶面 (110) 上丰富的 Co^{3+} 促进了 CO 的吸附及其随后与邻近表面氧作用形成 CO_2 的反应, 可在 -77 °C 时实现 1% CO 的完全转化. Hu 等^[6]采用水热法合成了以 (011) 为主要暴露晶面的 Co_3O_4 纳米带和以 (001) 为主要暴露晶面的纳米立方体, 发现 (011) 面上 Co^{3+} 对 CO 氧化反应性能较 (001) 面上高, 从而决定了以上两种纳米材料活性的差异. Ren 等^[7]以 KIT-6 为硬模板剂合成了介孔 Co_3O_4 , 在 400 °C 用 O_2 (8%) 预处理后, 可在 -50 °C 下实现 1% CO 的完全转化. 另一方面, 基于氧空穴及氧的活化对 Co_3O_4 催化氧化 CO 性能的重要作用^[8,9], 人们通过掺杂异质原子、在合适条件下进行预处理等方式可制得性能优异的催化剂. Luo 等^[10]考察了 Ce 取代对 Co_3O_4 催化氧化 CO 性能的影响, 发现 $\text{Co}/(\text{Co}+\text{Ce})$ 为 0.3 时性能最优, 并将其归因于该材料上高浓度氧空穴的形成. Lou 等^[11]的研究表明, Bi_2O_3 的添加导致了 Co_3O_4 表面氧空穴的形成, 因而其催化氧化 CO 反应的性能增加: 在 20% Bi_2O_3 - Co_3O_4 上, -89 °C 时可实现 1% CO 的完全转化, 在 -75 °C 时 100% 的 CO 转化可维持 10 h. Wang 等^[12]以 $\text{Co}(\text{NO}_3)_3$ 为钴源, 以 $(\text{NH}_4)_2\text{CO}_3$ 为沉淀剂, 采用沉淀法制备了 Co_3O_4 , 活性测

试与 O_2 程序升温脱附 (O_2 -TPD) 的结果表明, 表面 O_2^- 及 O^- 物种在 CO 的低温氧化反应中起重要作用. Sadykov 等^[9]研究发现, 350 °C 下 He 预处理引发的 Co_3O_4 的表面重构效应有利于弱吸附态氧物种的形成, 从而促进了 CO 的低温氧化. Yu 等^[13]的研究表明, 以空气、 N_2 、CO/空气预处理 Co_3O_4 有利于催化剂表面氧空穴的形成, 促进了分子氧的吸附与活化, 从而提高了其低温催化氧化 CO 的性能, 在 -80 °C 可实现 1% CO 的完全转化.

为优选 Co_3O_4 制备条件, 本文考察了焙烧温度对 Co_3O_4 催化氧化性能的影响; 同时以正电子湮没寿命谱, 程序升温脱附考察了预处理条件对 Co_3O_4 表面氧空穴的形成及其对氧吸附活化的影响.

2. 实验部分

2.1. Co_3O_4 的制备

采用沉淀法制备 Co_3O_4 ^[13,14]. 将加热至 70 °C 的 Na_2CO_3 溶液 (0.15 mol/L) 迅速倒入同温的 $\text{Co}(\text{NO}_3)_2$ 溶液 (0.12 mol/L) 中, 在 60~70 °C 搅拌 1 h, 冷却, 静置 2 h 后, 用大量的去离子水 (低于 70 °C) 洗涤, 离心分离沉淀物, 重复多次至上清液 pH 为 8.0 左右; 将所得沉淀物于 100 °C 干燥过夜, 在空气中于不同温度 (120~400 °C) 焙烧 4 h, 粉碎, 过筛 (60~90 目) 以备.

2.2. Co_3O_4 的评价

CO 氧化反应中, 催化剂用量为 150 mg, 反应气组成为: 1.0% CO, 20% O_2 , 79% N_2 , 水蒸气的含量为 0.018%. 气体总流量为 50 ml/min, 空速为 20000 ml/(h·g). 在活性测试之前, 催化剂样品均在指定的温度 (120~250 °C) 下于 N_2 (或空气) 中处理 40 min. 采用 GC8A 型气相色谱仪 (Shimadzu 公司) 检测反应前后 CO 的浓度, 并算得 CO 转化率. 当反应温度低于 0 °C 时, 以液氮冷却的甲醇控制反应温度.

2.3. Co_3O_4 的表征

催化剂的比表面积在 Quantachrome 公司的 Autosorb(IQ) 型吸附仪上测定. 测试之前, 样品在 120 °C 脱气处理 4 h. X 射线衍射 (XRD) 表征在 Panalytical 型 X 射线衍射仪 (X'Pert PRO MPD) 上进行, $\text{Cu K}\alpha$ 射线, 扫描范围 $2\theta = 10^\circ \sim 90^\circ$, 扫描步长 0.02° . 干燥样品的热重分析 (TG) 在岛津 TGA-50 分析仪上进行. 利用 HITACHI 公司的 H-7500 型电子透射显微镜 (TEM) 对样品进行表征, 加速电压 80 kV.

O_2 -TPD 实验在配备 QIC 20 质谱检测器 (Hiden, UK) 的全自动催化剂表征系统 (Autochem 2920, Micromeritics, USA) 上进行, 催化剂用量为 200 mg^[13]. 样品经不同条件的预处理后, 降温至 -70 °C 进行氧气吸附 1 h. 将气氛切换为 He 并吹扫系统 1 h (30 ml/min), 在相同气氛下以 10 °C/min 的速度升温至 600 °C. 其间, 以质谱检测 O_2 的信号 ($m/z=32$).

正电子湮没寿命谱 (PALS) 测定在中国科学院高能物理研究所核分析技术重点实验室进行, 采用的仪器为由 BaF_2 闪烁晶体探测器及核电子学插件组成的快-慢复合正电子湮没寿命谱仪. 谱仪时间分辨率 (FWHM) 为 190 ps. 两片相同的 Co_3O_4 样品将 ^{22}Na 源夹在中间, 置于两个探测器轴向中心. 测试前, 样品经不同条件的预处理, 测试时将样品和 ^{22}Na 源装在充有 N_2 的橡胶气球中, 以防止测试过程中水蒸气等的吸附引发催化剂表面性质如氧空穴的变化. 实验得到的寿命谱使用软件包 LT9.0 进行拟合.

3. 结果与讨论

3.1. Co_3O_4 前驱体分析

图 1 为经 100 °C 干燥过夜的 Co_3O_4 前驱体样品的 TG 和 DGT 曲线. 由图可见, 在 100~620 °C 样品失重 24.6%. 一般而言, 在以 Co^{2+} 为钴源, 以碳酸盐为沉淀剂合成 Co_3O_4 时, 未经焙烧的样品多为碱式碳酸钴 ($\text{Co}_2(\text{OH})_2\text{CO}_3$)^[15,16]. 该前驱体转化为 Co_3O_4 的理论失重量为 24.2%, 与本文结果相近, 表明未焙烧的样品中主要以 $\text{Co}_2(\text{OH})_2\text{CO}_3$ 的形式存在. 还可以看出, 250 °C 以上焙烧可以得到较为稳定的催化剂样品.

3.2. 焙烧温度对 Co_3O_4 结构与催化性能的影响

图 2 是在空气中于 120~400 °C 焙烧样品的 XRD 谱. 由图可见, 120 °C 焙烧时, $\text{Co}_2(\text{OH})_2\text{CO}_3$ 中部分羟基与碳酸盐发生脱除、分解, 已有立方相 Co_3O_4 形成 (JCPDS 42-1467), 同时还能观察到 $\text{Co}_2(\text{OH})_2\text{CO}_3$ 的衍射峰^[16]. 150 °C 焙烧的样品上仅能观察到 Co_3O_4 的特征峰. 随着

焙烧温度的继续升高, Co_3O_4 特征峰的衍射强度逐渐增强, 表明 Co_3O_4 结晶度愈高, 与 Wang 等^[12,17]的结果一致. 根据谢乐公式计算了不同温度下焙烧样品的粒径, 结果列于表 1; 同时还给出了各样品的比表面积. 可以看出, 随着焙烧温度的升高, 所得样品的比表面积逐渐降低, 粒径逐渐增大; 在 350 °C 及更高温度下焙烧时, 样品的比表面积大幅度降低、粒径尺寸迅速增大, 很可能对 Co_3O_4 催化氧化 CO 这一结构敏感型反应的活性产生明显影响^[1]. 需要指出的是, 120 °C 焙烧样品的比表面积最高, 但其颗粒尺寸也最大. 这是由于该样品中 Co_3O_4 与 $\text{Co}_2(\text{OH})_2\text{CO}_3$ 共存, 按前者计算粒径存在较大的误差.

图 3 为不同温度下焙烧样品的 TEM 照片. 由图可见, 焙烧后的 Co_3O_4 样品呈纳米级颗粒状, 尺寸分布较为均一; 200~300 °C 焙烧样品的粒径尺寸相差不大, 而 400 °C 焙烧时粒子明显增大, 与 XRD 结果吻合.

图 4 为不同温度下焙烧的 Co_3O_4 样品催化氧化 CO 反应性能. 前已提及, 预处理气氛与温度能显著改变 Co_3O_4 催化氧化 CO 的性能^[13]. 为了消除预处理条件的影响, 所有样品均用 150 °C 下 N_2 预处理 40 min 后进行活性测试 (120 °C 焙烧样品例外, 该样品在 120 °C 预处理, 以防止过高的预处理温度对催化剂结构的影响). 由图可见, 120 °C 焙烧的样品活性较低, 在 100 °C 以上时才能将 1% CO 完全转化. 这可能与 Co_3O_4 及 $\text{Co}_2(\text{OH})_2\text{CO}_3$ 共存相关. 在 200~300 °C 焙烧的 Co_3O_4 呈现出优异的催化氧化 CO 性能, 在 -80 °C 时 CO 转化率均达到 100%; 继续升高焙烧温度, 所得样品的活性大幅度降低.

为了更清楚地描述焙烧温度对催化剂结构与性能的影响, 图 5 示出不同温度下焙烧样品的比表面积与 CO 转化率为 50% (T_{50}) 的对应关系. 很明显, Co_3O_4 (150~400 °C 温度焙烧) 的催化活性与其比表面积存在明显的差别: 150~300 °C 焙烧时, 所得样品的比表面积与 T_{50} 近于平行关系; 300 °C 以上焙烧时, 样品的比表面积迅速降低, 但其 T_{50} 大幅度升高. 这与 Wang 等的结果一致^[12,17].

3.3. 预处理条件对 Co_3O_4 表面氧空穴形成及其低温催化氧化 CO 性能的影响

近些年来, PALS 已成为研究固体材料原子尺度空穴的强有力工具^[18,19]; 并已成功应用于以氧空穴为代表的催化材料活性结构研究^[20-22]. 为了深入研究预处理方式对 Co_3O_4 表面氧空穴形成及其对催化氧化 CO 性能的影响, 进行了 PALS 表征, 结果如表 2 所列. 由表可见, 300 °C 焙烧及不同气氛预处理后的 Co_3O_4 表面存在三种不同大小的空穴^[21]: 其中, 寿命最长的 τ_3 (2.08~3.27 ns) 为正

电子在 Co_3O_4 微孔洞中的湮没; τ_1 可归属为正电子在以 $\text{Co}^{2+}-\square-\text{Co}^{2+}$ 形式存在的氧空穴中的湮没(下文简称为单氧空穴),其寿命为 190~223 ps. 该空穴的形成可能源于两配位表面氧原子($\text{Co}^{2+}-\text{O}-\text{Co}^{3+}$)的脱除^[4,23]. τ_2 (寿命为 361~420 ps)为氧原子空穴团,如单氧空穴的二聚体,三聚体或更大空穴团.

表 2 还给出了不同空穴的相对浓度,以 I_1, I_2, I_3 表示,分别对应单氧空穴(τ_1),氧空穴团(τ_2)及微孔洞(τ_3)的相对含量. 与 300 °C 空气气氛中焙烧的 Co_3O_4 样品相比,预处理对微孔洞的尺寸和相对含量的影响不大,但对单氧空穴及其团簇产生明显影响. 150 °C 空气预处理后, τ_2 有所增大,但其相对浓度没有明显改变. 与未预处理的样品相比, 150 °C 下 N_2 预处理对空穴大小的影响并不明显,却显著提高了空穴团的相对浓度(I_2),而单氧空穴相对浓度(I_1)明显降低. 预处理温度升高时, I_2 继续增大, I_1 值持续降低, 250 °C 预处理后 I_2 值高达 71.2%. 这清楚表明,对焙烧后的 Co_3O_4 进行合适温度下 N_2 预处理能明显提高氧空穴团的相对浓度,而这是以单氧空穴相对浓度的降低为代价.

Xie 等^[5]在研究 Co_3O_4 纳米棒催化氧化 CO 时提出,催化剂暴露晶面上的 Co^{3+} 在 CO 吸附及随后与邻近表面氧作用形成 CO_2 的反应中起到关键作用. 邻位氧原子的脱除导致了 Co_3O_4 表面氧空穴的形成,在气相氧分子的作用下,表面氧得到补充,活性位 Co^{3+} 得以恢复,从而保证了整个反应的顺利进行. Yu 等^[13]则认为, Co_3O_4 纳米颗粒表面氧空穴的稳定存在是活化氧分子、催化氧化 CO 的关键. 为了验证以上两种不同的反应机制, Jiang 等^[23]利用 DFT+U 模拟研究了 $\text{Co}_3\text{O}_4(110)$ 面氧空穴的形成与 CO 氧化反应途径. 模拟研究表明, $\text{Co}_3\text{O}_4(110)$ 面上两配位氧原子迁移至邻位单氧空穴的能垒仅为 0.26 eV,表明氧空穴具有较强的移动性,从而导致氧空穴团(如双空穴)的形成. 他们同时指出,由两个相邻的两配位氧原子脱除形成 O_2 的能垒约为 5 eV,而 150~250 °C 预处理不足以克服该能垒,因此认为该温度下预处理难以导致表面氧空穴的形成. 但是,该模拟研究忽略了以下两个因素: (1) 没有考虑焙烧样品上一定浓度单氧空穴的存在,而这已由 PALS 的表征所证实,因此也就忽略了合适气氛(如 N_2) 预处理条件下单氧空穴迁移复合导致氧空穴团相对浓度增加的可能性; (2) 忽略了预处理过程中,因单氧空穴邻位氧原子的脱除导致氧空穴团的形成,而这一反应的能垒应远低于两个相邻的氧原子脱除形成氧空穴所需能量^[24],因此也就不能合理解释本文采用的

预处理条件在氧空穴形成中的作用. 基于上述分析,我们认为,合适温度下的 N_2 预处理导致了 Co_3O_4 表面单氧空穴的迁移与集聚,抑或是在已有单氧空穴的邻位发生氧原子的脱除,导致了空穴的长大,以及氧空穴团相对浓度的升高,其可能作用机制如图式 1 所示.

Mitsui 等^[25]的研究表明,即使是 Pd(111) 上 H_2 发生解离的反应,也需要三个或更多个 H 原子空穴团的参与,可见空穴团在催化反应中的重要作用. Jiang 等^[22]量化模拟的研究也表明, $\text{Co}_3\text{O}_4(110)$ 面氧空穴的二聚体较单个氧空穴更有利于氧分子的吸附与活化,从而促进了 CO 氧化反应的进行. 鉴于此,图 6 为不同预处理条件下 Co_3O_4 表面氧空穴团的相对浓度(I_2)与吸附态氧含量的对应关系. 其中,吸附态氧的相对含量由低温 O_2 -TPD 实验测定^[13]. 可以看出, Co_3O_4 表面氧空穴团浓度的增加导致了吸附态氧含量的增加,尤其是不同温度下 N_2 预处理后, I_2 与吸附态氧的量存在明显的线性关系,这凸显了表面氧空穴在 O_2 吸附与活化中的关键作用.

已有的研究表明^[26], Co_3O_4 上低温氧化 CO 的反应很可能遵循分子氧机理,因预处理温度与气氛的调变引发的表面氧空穴及其对分子氧吸附的改变,理应导致其催化氧化 CO 性能的改变. 图 7 为不同气氛与温度预处理样品在 0 °C 催化氧化 CO 的活性. 150 °C 空气预处理后, 0 °C 反应时 100% CO 转化率可维持 37 h,随后随着反应时间的延长 CO 转化率降低. 这可能是由于随着反应的进行,氧空穴等活性位被反应过程中形成的碳酸盐所占据^[23]. 另一方面, Co_3O_4 催化氧化 CO 的性能对水蒸气的存在非常敏感,随着反应的进行,反应气中共存的水分子在催化剂的表面,如氧空穴上发生吸附,也会导致活性的逐渐降低^[13,14]. 在 150 °C 氮气预处理的样品上, 0 °C 时 CO 完全转化可持续 69 h; 当预处理温度升高到 200 °C 时,所得样品上 CO 的完全转化可维持 90 h.

图 8 进一步给出了不同预处理后,催化剂表面吸附态氧的量与 CO 氧化性能的关系. 很明显,催化剂表面吸附态氧的量越多,其催化氧化 CO 的活性愈持久. 这表明,表面氧空穴团在吸附活化氧分子的同时,也能吸附碳酸盐和水分子. 表面氧空穴团的浓度越高,其吸附碳酸盐 and 水的容量也越大,从而延缓了上述物种对氧气吸附活化以及 CO 催化氧化的抑制效应,使催化剂呈现出更优异的耐久性. 以上结果进一步验证了 Co_3O_4 表面氧空穴在吸附活化氧和低温催化氧化 CO 中的关键作用.

同时,我们也对失活后的催化剂重新进行预处理,然后测定其催化氧化 CO 的活性,结果见图 7. 可以看出,将

Co_3O_4 催化剂重新在 150 °C 用 N_2 预处理, 0 °C 时其催化氧化 CO 的活性得以恢复. 这可能是由于预处理时吸附于催化剂表面氧空穴团的碳酸盐和水等物种发生脱附, 氧空穴位得以恢复再生, 从而使催化剂重新具备了吸附活化氧及催化氧化 CO 的能力. O_2 -TPD 结果也表明 (图 7 中的插入图), 氧空穴可稳定存在于 Co_3O_4 表面, 经预处理可实现氧吸附性能的再生, 这很好地解释了其催化氧化 CO 活性的可恢复性.

4. 结论

Co_3O_4 低温催化氧化 CO 反应是一颗粒尺寸与表面

氧空穴敏感反应. 采用沉淀法制备的 Co_3O_4 颗粒尺寸及比表面积与焙烧温度密切相关, 在 150~300 °C 焙烧的样品具有较高的比表面积, 较小的颗粒尺寸, 因而具备了优异的低温催化氧化 CO 的活性. Co_3O_4 催化氧化 CO 的耐久性与表面氧空穴团的含量呈正相关. 合适温度 (150~250 °C) 下 N_2 预处理促进了 Co_3O_4 表面氧空穴团的形成, 提高了吸附与活化分子氧的能力, 延长了其催化氧化 CO 的耐久性. 同时, 重新预处理可使反应失活的 Co_3O_4 催化剂吸附分子氧的能力得以恢复, 使其催化氧化 CO 的活性得以再生, 进一步确认了氧空穴在 Co_3O_4 低温催化氧化 CO 中的关键作用.

2nd International Congress on Catalysis for Biorefineries (CatBior 2013)

September 22–25, 2013, Dalian, China

<http://catbior2013.dicp.ac.cn>

Call For Papers

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The Organizing Committee cordially invites you to participate in the 2nd International Congress on Catalysis for Biorefineries to be held in Dalian from 22nd to 25th September, 2013. The International Congress on Catalysis for Biorefineries originated in Torremolinos, Málaga, Spain in 2011. The congress alternates worldwide in odd years. This international congress aims to create a platform for the scientific exchange of the views and latest research findings in the development of clean and efficient processes for the catalytic conversion of biomass into fuels and chemicals.

2. Scopes

This congress is devoted to fundamental and applied research on catalytic processes for biomass transformation without enzymatic process. The topical areas of interest include, but are not limited to:

- Catalytic transformation of cellulose, hemicellulose, lignin, and raw biomass.
- Catalytic transformation of carbohydrates and sugar-derived products.
- Catalytic transformation of oil, fats, algae and oleo-derived chemicals.
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3. Publications

The most significant and original works will be selected for publication in the special issues of *Catalysis Today* (<http://www.journals.elsevier.com/catalysis-today/>) and *Chinese Journal of Catalysis* (<http://www.sciencedirect.com/science/journal/18722067>) after a peer-review process.

Key Dates:

- Online abstract submission: February 1st, 2013
- Deadline for submission of abstracts: April 1st, 2013
- Abstract acceptance notification: May 1st, 2013
- Deadline for early bird registration: July 1st, 2013
- Conference: September 22nd–25th, 2013

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