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Article

Structural changes of Rh-Mn nanoparticles inside carbon nanotubes studied by X-ray absorption spectroscopy

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ABSTRACT

Supported Rh-based catalysts such as Rh-Mn nanoparticles (NPs) have potential use in the synthesis of ethanol from syngas. The structure of Rh-Mn NPs in multi-walled carbon nanotubes under different atmospheres and temperatures was studied by X-ray absorption spectroscopy (XAS). TEM images showed that the NPs dispersed in the carbon nanotubes had a uniform size of 2 nm. XAS data revealed that the Rh-Mn NPs before reduction were composed of Rh_2O_3 clusters and mixed Mn oxide species. After reduction in a 10% H_2 -90% He atmosphere, the mixed Mn oxides were converted into nearly pure MnO. In contrast, the Rh_2O_3 clusters were easily decomposed to metallic Rh clusters even under a He atmosphere at 250 °C. The Rh clusters remained in the metal state under the next reduction atmosphere, but their dispersion in the Rh-Mn NPs increased with increasing temperature. No significant Mn-Rh or Mn-O-Rh interaction in the reduced NPs was observed in the extended X-ray absorption fine structure analysis. The results showed that there was no interaction between the MnO particles and Rh clusters and the role of the Mn promoter was mainly to improve Rh dispersion.

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1. Introduction

The synthesis of ethanol from syngas has received attention in recent years for its use as an alternative fuel to reduce the global dependence on petroleum [1–4]. The conversion of biomass to syngas by a catalytic process provides a promising alternate route to synthesize ethanol on a large scale [5]. Although a large amount of research on this synthesis route has been done, there is as yet no commercial process due to the existing challenges [6]. A growing consensus is that a supported Rh catalyst could be the most suitable catalyst for this catalytic conversion route because supported Rh particles can simultaneously adsorb CO in both molecular and dissociated states,

but the catalytic performance up to now is poor [7,8]. In order to enhance the catalytic activity of Rh, numerous methods have been tried, such as using a suitable support and adding promoters [9–18]. Recently, confining Rh or Rh-based nanoparticles in a limited space, such as in a zeolitic material or carbon nanotubes (CNTs), was shown to be an effective approach to improve the yield and selectivity for ethanol production from syngas [19–25].

Mn is a common promoter widely added to Rh to form supported Rh-Mn catalysts. A substantial amount of work has been carried out to investigate the promoting effects of Mn in the supported Rh-Mn catalysts [26–28]. However, there is still uncertainty about the state of Mn and the interaction between Mn

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and Rh in Rh-Mn catalysts. Wilson et al. [29] showed that Mn species exist as Mn^{2+} together with Rh^+ on a silica support. It has been found that Mn oxides cannot be completely reduced to metallic Mn in Rh-Mn catalysts [30]. In contrast, Luo et al. [31] found that Rh promoted the reduction of Mn oxides. In addition, it was proposed that the promoter Mn exists with Rh in a binary alloy [27]. Therefore, the determination of the chemical state of the Mn promoter and clarification of the interaction between Mn and Rh are critical for understanding the promoting effects of Mn in supported Rh-Mn catalysts. X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS), is a useful tool for this research. They can provide information about the electronic structure of the absorbing atoms and the local geometric structure surrounding the central absorbing atoms [32]. Besides, the XAS technique also can selectively detect an element and can be used for in situ measurement [33], so it is highly suitable for the study of the structure of Rh-Mn catalysts under a reduction atmosphere.

In this work, we used a supported Rh-Mn catalyst whose Rh-Mn nanoparticles (NPs) were inside multi-walled CNTs (MWCNTs) with nominal loading (mass fraction) of 5% Rh and 5% Mn, denoted as Rh-Mn@CNT, and investigated the structure of the Rh-Mn NPs by XAS analysis. Structural information of the Rh-Mn@CNT catalyst under a reduction atmosphere (10% H_2 or 10% CO balanced with He), such as the chemical states of Mn and Rh and the interaction between Mn and Rh, was extracted by analyzing the Mn and Rh K-edge XAS data. The results provide information for understanding the structure of Rh-Mn catalysts under reaction conditions and the promoting effects of Mn during ethanol synthesis from syngas over the supported Rh-Mn catalysts.

2. Experimental

2.1. Preparation of catalyst

Rh-Mn NPs in CNT channels as a catalyst for the production of ethanol from syngas were synthesized by a wet chemistry method described in a previous paper [19]. MWCNTs with 4–8 nm inner diameter and 250–500 nm length were used as a vessel to hold the Rh-Mn NPs.

2.2. TEM characterization

Transmission electron microscope (TEM) images were obtained using a FEI Tecnai G2 F20 S-TWIN TEM operated at an accelerating voltage of 200 kV. TEM grids were prepared by loading the sample dispersed ultrasonically in ethanol onto a copper grid.

2.3. XAS measurement and data analysis

The XAS data were collected on beam line BL14W1 at the Shanghai Synchrotron Radiation Facility. The electron storage ring was operated at 3.5 GeV. A double Si(111) or Si(311) crys-

tal monochromator was employed for energy selection. Mn K-edge XAS data of the catalyst were acquired in transmission mode while the Rh K-edge XAS data were acquired in fluorescence mode by using a 32-element Ge solid state detector. XAS data of Rh foil, Rh_2O_3 , Mn foil, MnO, and Mn_2O_3 were also measured under a similar condition for reference. An in situ cell was employed for collecting in situ XAS data under ordinary pressure in different atmospheres at different temperatures. The in situ cell was modified from a commercial Linkam T95 device (purchased from Linkam Scientific Instruments Ltd). An appropriate amount of catalyst and LiF powder was uniformly mixed, and then the mixture was crushed and formed into a pellet by using a rubber sheeter. The sample was processed by atmospheres in the order of He, 10% H_2 -90%He, and 10% CO-90% He. Under each atmosphere, the temperature was increased from room temperature (RT) to 300 °C followed by annealing from 250 °C to RT before changing the atmosphere. The flow rate of gas was 80 mL/min. The rate of the heating was 5 °C/min and the time of heating at the final temperature was 1 h prior to the XAS scan. XAS data analysis was carried out using the Ifeffit software package [34]. The normalized EXAFS function, $\chi(E)$, was transformed from energy space to k -space, $\chi(k)$, where k is the photoelectron wave vector. The $\chi(k)$ data were multiplied by k^2 to compensate for the damping of EXAFS oscillations in the high k -region. The backscattering amplitude and phase shift were obtained from theoretical calculation using the FEFF code (version 6.0) [32]. S_0^2 values of 0.65 and 0.85 were obtained from fitting to MnO and Rh standard samples. From the analysis, structural parameters, such as the coordination number (N), bond distance (R), Debye-Waller factor (σ^2), and inner potential shift (ΔE_0), could be calculated.

3. Results and discussion

The detailed TEM characterization of the Rh-Mn@CNT catalyst was reported in a previous paper [19]. Here, the TEM technique was used to confirm the presence of Rh-Mn NPs inside the CNTs. The TEM image of the Rh-Mn@CNT catalyst is shown in Fig. 1, which showed that the Rh-Mn NPs were well dispersed inside the CNT channels with a uniform size of approximately 2 nm.

The catalytic reactions are normally performed at an industrial temperature and in an industrial atmosphere. In order to

Fig. 1. TEM image of the Rh-Mn@CNT catalyst.

investigate the actual working chemical state and local geometric structure of both Mn and Rh, we performed in situ XAS measurements under different atmospheres at different temperatures. Prior to the XAS measurements, the as-synthesized sample was kept in air. The representative Mn K-edge XAS data in the energy range from 6339 to 7339 eV is shown in Fig. 2(a). There was a small jump above the edge at ~ 7100 eV, which implied the presence of Fe impurity. Further Fe K-edge XANES data showed that its curve is similar to that of Fe_2O_3 (Fig. 2(b)). This finding revealed the existence of impurity Fe in the form of Fe oxide. This minor amount of Fe oxide may be from the preparation of the CNTs. In order to exclude the interference of Fe, we chose 7050 eV as the upper limit of the X-ray photon energy for collecting the Mn K-edge EXAFS data.

To better understand the influence of a H_2 atmosphere on the structure of the Rh-Mn NPs, the stability of these NPs in the noble gas should be examined, and small molecules adsorbed on their surfaces such as H_2O molecules should be removed. So we also performed XAS measurements for the Rh-Mn@CNT sample in He at different temperatures. The Mn K-edge XANES spectra of the Rh-Mn@CNT catalyst in a He atmosphere at different temperatures are shown in Fig. 3(a). The appearance of a pre-edge peak at 6540.7 eV indicated that most Mn species existed in the form of Mn oxides [35]. Significantly, these XANES spectra have a broad main edge crest, which suggested the existence of different kinds of Mn oxide phases (MnO_x).

Fig. 2. (a) Mn K-edge XAS spectra of Rh-Mn@CNT; (b) Fe K-edge XANES spectra for Rh-Mn@CNT and the reference of Fe_2O_3 .

Fig. 3. (a) Mn K-edge XANES spectra for Rh-Mn@CNT in a He atmosphere at different temperatures; (b) Comparison of the FT of the Mn K-edge EXAFS spectra with that of MnO.

There was an obvious difference between the spectrum collected at RT and that at 120 °C, which can be attributed to the removal of adsorbed H_2O molecules. Moreover, these broad main edge crests showed a similar shape, which proved that the mixed Mn oxide phases were stable under the He atmosphere. With increasing temperature, the edge position showed a minor shift to low energy, which can be attributed to the partial reduction of the Mn oxides. The Fourier transform (FT) of the EXAFS data is shown in Fig. 3(b). The Fourier transformed EXAFS spectra of Rh-Mn@CNT have similar features, which showed that there was no apparent change in the local structure of Mn. The peak at 2.7 Å can be attributed to the Mn-O-Mn contribution. Its intensity decreased with increasing temperature, indicating the increase of disorder. These FT data could not be explained by a simple structural model. The intensity of the peaks at 2.7 Å was quite weak, showing that the MnO_x were amorphous.

After a thermal treatment in a He atmosphere, the sample was further treated in 10% H_2 -90% He atmosphere at different temperatures. The Mn K-edge XANES data are shown in Fig. 4(a). With the temperature increase, the broad main edge crest became narrower and the edge position showed a small shift to low energy. These results implied some reduction and that the mixed MnO_x phases were changed to a pure phase. In addition,

Fig. 4. (a) Mn K-edge XANES spectra for Rh-Mn@CNT in an atmosphere of 10% H₂-90% He at different temperatures; (b) Comparison of the FT Mn K-edge EXAFS spectra with those of MnO and Rh-Mn@CNT under an annealing treatment at 250 °C (AN_250) and 200 °C (AN_200); (c) Mn K-edge XANES and (d) the corresponding k^2 -weighted $\chi(k)$ data for MnO, Mn₂O₃, and AN_200.

the intensity of the peak at 6569 eV also increased with temperature, indicating more ordered structure in the medium and long range environment. It should be noted that the pre-edge peak at 6540.7 eV was independent of the temperature, which agreed with that the pre-edge feature of the Mn oxides was much less affected by changes in the medium and long range environment than the edge region. The Fourier transformed Mn K-edge EXAFS data of the sample in 10% H₂-90% He atmosphere at different temperatures are shown in Fig. 4(b). The peaks at 1.7 and 2.7 Å are the Mn-O and Mn-O-Mn contributions, respectively. At temperatures below 250 °C, the EXAFS spectra were similar to those in a He atmosphere. It is significant that when the temperature was above 250 °C, the EXAFS spectra were similar in character to that of MnO, which has peaks at 1.7, 2.7, 4.8, and 5.8 Å. This phenomenon is more obvious for the sample annealed at 200 and 250 °C (pattern AN_200 and AN_250), which suggested that most Mn atoms in reduced Rh-Mn@CNT were in the MnO form. Although it is difficult to determine the redox state of Mn by only using the Mn K-edge position [35], there is an approximate linear correlation between the K-edge position and the redox state of simple Mn oxides, such as MnO, Mn₃O₄, Mn₂O₃, and β-MnO₂ [36,37]. It is possible to determine the oxidation state of closely related compounds by the comparison with the standard samples [38]. The comparison of the Rh-Mn@CNT sample annealed at 200 °C

(AN_200) with the MnO and Mn₂O₃ samples is shown in Fig. 4(c). The Mn K-edge position and shape of AN_200 were close to that of MnO, implying that most Mn species in reduced Rh-Mn@CNT were Mn²⁺. In addition, the EXAFS oscillation of the AN_200 sample has a similar frequency but with lower amplitude in comparison with that of MnO (Fig. 4(d)). The lower oscillation amplitude was due to the small size of the Rh-Mn NPs and the increase in disorder at higher temperature. The above results and analysis demonstrated that the chemical state of the promoter Mn was close to +2 for the Rh-Mn@CNT catalyst under the 10% H₂-90% He atmosphere at 300 °C. This result is consistent with the widely accepted view that MnO is difficult to reduce to metallic Mn even when placed in contact with Rh [30,39]. Moreover, in the H₂-TPR result reported by Li et al. [24], the Mn/CNT catalysts with MnO_x particles between 10 and 40 nm showed two redox peaks at 290 and 410 °C from the reduction of MnO₂ or Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO, respectively. For our Rh-Mn particles, the lower reduction temperature may arise from the smaller MnO_x particles. In the EXAFS spectra, there was no peak from reduced Rh-Mn@CNT that could be attributed to Mn-O-Rh and Mn-Rh contributions, indicating that there was no significant interaction between Mn and Rh. We concluded that the mixed MnO_x phases can be reduced to MnO species by H₂ at temperatures above 250 °C.

In addition, Rh K-edge XAS data of the Rh-Mn@CNT catalyst

Fig. 5. (a) Rh K-edge XANES spectra for Rh-Mn@CNT in a He atmosphere at different temperatures and the references of Rh foil and Rh₂O₃; (b) FT Rh K-edge EXAFS spectra.

under different atmospheres and temperatures were also collected. The XANES spectra for Rh-Mn@CNT in a He atmosphere at different temperatures are shown in Fig. 5(a). The first absorption peak centered at 23240 eV in the main edge region is from the transition of electrons from the 1s states to unoccupied *p* orbitals [40]. Therefore, any variation in the oxidation state will be reflected in the intensity of the first absorption peak. Figure 5(a) shows that the initial Rh-Mn@CNT sample at RT has an obvious peak at 23240 eV, indicating the oxidation state of Rh. The Rh K-edge position of the sample both at RT and 150 °C was close to that of Rh₂O₃, further revealing the presence of RhO_x. The edge position shifted to be close to that of Rh foil when the temperature reached 250 °C, revealing the formation of metallic Rh. The first peak (23236 eV) above the edge for the Rh-Mn@CNT sample at 300 °C was very similar to that of Rh foil, indicating that there was no significant electronic effect induced by the presence of Mn, which was similar to the result of Schwartz et al. [28]. This result was further confirmed by later EXAFS analysis. Moreover, the sample at 300 °C has a smaller peak at 23260 eV in comparison to the Rh foil as a result of the small size of the metallic Rh particles. This result showed that the oxidized Rh particles were not stable and can be decomposed to metallic Rh particles in He when the temperature reached 250 °C. A similar result was observed by H₂-TPR data, that is, Rh₂O₃ is not very stable and can be reduced by H₂ at a relatively low temperature (about 150 °C) [41,42]. The formation of metallic Rh particles was further confirmed by the formation of Rh-Rh coordination at 2.5 Å accompanying with much decreased Rh-O coordination at 1.5 Å (Fig. 5(b)). This result further demonstrated that Rh oxide was converted to metallic Rh and clearly indicated that the Rh-O interaction was relatively weak and can be decomposed in a He atmosphere above 250 °C. There was no observable peak that can be attributed to a Rh-Mn contribution, which indicated the absence of a Rh-Mn bimetallic alloy. We concluded that RhO_x will be decomposed to metallic Rh under He when the temperature is above 250 °C.

After the thermal treatment in a He atmosphere, the sample was further reduced in a 10% H₂-90% He atmosphere followed

by a thermal treatment in a 10% CO-90% He atmosphere. The Rh K-edge XANES spectra of the sample under the different reduction atmospheres from 150 to 300 °C have the same shape (Fig. 6). The result showed that the local electronic structure of Rh has no significant change and Rh was maintained in the metal state. In contrast, the corresponding FT of the EXAFS spectra showed some dependence on the temperature (Fig. 7). The second peak at 2.5 Å was attributed to the Rh-Rh contribution. Figure 7(a) shows that the second peak gradually decreased with temperature from RT to 300 °C, which indicated the increase of both the disorder and dispersion of Rh particles at higher temperature. In the case of the 10% CO-90% He atmosphere (Fig. 7(b)), the second peak showed a similar trend but without a regular pattern as compared to that in Fig. 7(a). These results revealed an obvious improvement in the dispersion of the Rh particles in the Rh-Mn NPs at 300 °C under the reduction atmosphere.

The structural parameters from fitting the Mn K-edge and Rh K-edge EXAFS data are given in Table 1. The results showed that the bond lengths of Mn-O and Mn-O-Mn in the Rh-Mn@CNT catalyst after reduction (AN_200) were close to

Fig. 6. Comparison of Rh K-edge XANES data for Rh-Mn@CNT in 10% H₂-90% He ((1)–(4)) with 10% CO-90% He ((5)–(8)) at 150 ((1) and (5)), 200 ((2) and (6)), 250 ((3) and (7)), and 300 °C ((4) and (8)).

Fig. 7. (a) FT Rh K-edge EXAFS data in 10% H₂-90% He and (b) in 10% CO-90% He at different temperatures.

those of MnO. In addition, the coordination number (N) of the Mn–O was 5.3 ± 0.5 , which was close to that of bulk MnO, indicating that most Mn atoms were coordinated with O. In contrast, the N of the Mn–O–Mn shell was 8.5 ± 1.5 , which was much lower than that of MnO whose N of the Mn–O–Mn shell is 12. This result indicated that the MnO particles in reduced Rh-Mn@CNT have a very small size. Similarly, the Rh-Mn@CNT catalyst before reduction (RT_He) has similar bond length of both Rh–O and Rh–O–Rh in comparison with Rh₂O₃. The low N of the Rh–O–Rh shell suggested that the Rh atoms existed in the form of Rh₂O₃ clusters. For the Rh-Mn@CNT catalyst after reduction (RT_H₂), the N obtained for the Rh–Rh shell was 5.3 ± 0.8 , which is much smaller than that of Rh foil. This result is an indication of highly dispersed metallic Rh in the catalyst. The average size of these Rh particles was estimated to be less than 1 nm from Rh cluster models with varying numbers of atoms [43,44]. In addition, no significant Rh–Mn or Rh–O–Mn interaction was observed. Together with the above TEM result, we can also estimate that the average size of the MnO particles was between 1 and 2 nm.

In summary, there was no significant Mn–Rh or Mn–O–Rh bonding from the XAS analysis, which suggested that there is no significant chemical interaction between the MnO particles and the Rh clusters even though they were in physical contact. Moreover, when Rh-Mn@CNT was placed under a 10% H₂-90% He atmosphere from 250 to 300 °C, the size of the MnO parti-

cles showed a significant increase, and the size of the Rh clusters showed an obvious decrease. This is indicative of the promotion for the dispersion of metallic Rh clusters by the MnO particles. Accordingly, the promoter Mn improved the Rh dispersion.

4. Conclusions

The structure of Rh-Mn NPs confined in MWCNTs (Rh-Mn@CNT) was studied by XANES and EXAFS. The Rh-Mn nanoparticles were distributed in CNT channels with a uniform size of 2 nm. Before reduction, the Mn and Rh species existed in the form of MnO_x and Rh₂O₃ clusters, respectively. Under a reduction atmosphere, the MnO_x species were reduced to MnO as a stable oxide, and the Rh₂O₃ clusters were not stable and were decomposed to Rh clusters even under a He atmosphere at 250 °C. The Rh clusters were stable and remained in the metallic Rh state in an atmosphere of 10% H₂ or 10% CO balanced with He. No interaction between Rh and Mn in reduced Rh-Mn@CNT was observed.

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Table 1

Structural parameters from the EXAFS spectra at the Mn K-edge and Rh K-edge for Rh-Mn@CNT.

Sample ^a	Path	N	R (Å)	σ^2 (10^{-3} Å ²)	ΔE_0 (eV)
RT_He	Rh–O	4.6 ± 0.4	2.06 ± 0.01	2.4 ± 0.9	0.8 ± 0.9
	Rh–O–Rh	1.4 ± 0.6	2.76 ± 0.02	5.8 ± 2.8	9.1 ± 2.6
RT_H ₂	Rh–O	1.1 ± 0.4	2.06^b	6.0^b	2.3
	Rh–Rh	5.3 ± 0.8	2.67 ± 0.01	4.2 ± 0.9	-9.5 ± 1.1
AN_200	Mn–O	5.3 ± 0.5	2.19 ± 0.01	10.3 ± 1.4	3.4
	Mn–O–Mn	8.5 ± 1.5	3.15 ± 0.01	17.1 ± 1.9	-1.7

^a RT_He, RT_H₂, and AN_200 represent the Rh-Mn@CNT samples in He atmosphere at RT, in 10% H₂-90% He atmosphere at RT, and in 10% H₂-90% He atmosphere under annealing treatment at 200 °C, respectively.

^b This value is set to get a better fitting.

Graphical Abstract

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Rh-Mn nanoparticles in reduced Rh-Mn@CNT catalyst comprise metallic Rh and MnO that do not have significant interaction.

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X射线吸收谱研究碳纳米管内Rh-Mn纳米粒子结构的变化

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摘要: 利用X射线吸收谱技术研究了负载于多壁碳纳米管内的Rh-Mn纳米粒子在不同气氛和温度下的结构。结果表明, Rh-Mn粒子在空气中是由氧化铑团簇和混合锰氧化物组成。经过氢气在300 °C下还原后, 混合锰氧化物种转化成MnO。而氧化铑团簇在He气氛下当温度达到250 °C时就会发生分解而形成金属铑团簇。对形成的铑团簇用H₂或CO进行热处理, 发现其分散性随温度升高而提高; 同时, X射线吸收谱实验没有观察到Mn和Rh之间存在显著的相互作用, 助剂Mn的主要作用是提高了Rh的分散性。

关键词: 铑; 锰; 纳米粒子; X射线吸收近边结构; 扩展X射线吸收精细结构

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1. 前言

乙醇用于燃料可以降低地球对石油的依赖, 最近几年合成气制乙醇得到了重点关注^[1-4]. 催化转化生物质制合成气为这一途径大规模合成乙醇提供了潜在机会^[5]. 虽然对这一合成方法进行了大量研究, 但一直还没有进入商业化生产^[6]. 一个共同的认识是负载型Rh粒子可以同时以分子和解离形式吸附CO, 但是存在的问题是催化性能不好^[7,8]. 为了增强Rh的催化性能, 研究人员在选择合适的载体和添加不同助剂等方面做了大量工作^[9-18]. 最近, 研究发现将Rh或Rh基纳米粒子限制在某些空间内, 例如分子筛材料和碳纳米管等, 可以有效提高合成气制乙醇的产率和选择性^[19-25].

Mn作为一种常用助剂被广泛添加到Rh中形成Rh-Mn催化剂. 许多工作研究了Mn在负载型Rh-Mn催化剂上的增强活性效应^[26-28]. 然而, 对Mn的化学态及Mn与Rh之间的相互作用还不清楚. Wilson等^[29]发现, Mn以Mn²⁺和Rh⁺共存在氧化硅载体上. 而且, 研究还发现Rh-Mn催化剂中的Mn氧化物不能够被完全还原成金属Mn^[30]. 相比之下, Luo等^[31]发现, Rh可以促进Mn氧化物的还原. 除此之外, 研究还发现助剂Mn是以双金属合金的形式与Rh共存的^[27]. 因此, 确定助剂Mn的化学态和辨识Mn与Rh之间的相互作用对于认识Mn的提高效应就显得很关键. X射线吸收谱(XAS), 包括X射线吸收近边结构(XANES)和扩展X射线吸收精细结构(EXAFS), 是一种材料研究的有用工具, 它可以提供吸收原子的电子结构和周围的局域几何结构^[32]. 此外, XAS技术还具有元素分辨特性且可用于原位条件下的研究^[33]. 因此, 它很适合对反应气氛下的Rh-Mn催化剂进行研究.

我们选用Rh-Mn负载型催化剂作为实例, 利用XAS方法系统地研究了Rh-Mn粒子的结构; 这里的Rh-Mn粒子中的Rh和Mn在催化剂中的质量分数均为5%. 粒子负载在多壁碳纳米管内, 标记为Rh-Mn@CNT. 我们利用Mn和Rh的K边XAS数据研究了它们在不同化学气氛下的化学态及其相互作用. 实验结果为理解反应条件下的Rh-Mn粒子结构和Mn的增强效应提供了互补信息.

2. 实验部分

2.1. 催化剂制备

催化剂样品通过湿化学方法制得, 文献^[19]中有详细描述. 所用多壁碳纳米管的长度为250–500 nm, 内径为4–8 nm.

2.2. TEM表征

Rh-Mn@CNT的透射电镜(TEM)照片通过FEI Tecnai G2 F20 S-TWIN透射电镜获得, 使用的加速电压是200 kV. TEM样品的制备是将待测样品分散在乙醇中, 然后滴在铜网上在空气中自然干燥.

2.3. XAS实验测量和数据处理

XAS数据是在上海光源BL14W1线站上采集的. 电子储存环的运行能量为3.5 GeV. 单色器使用Si(111)或Si(311)两套晶体. Mn K边XAS数据利用透射模式采集, Rh K边XAS数据利用荧光模式采集(32元Ge固体探测器). 为了进行比较, 还测量了Rh箔、Rh₂O₃、Mn箔、MnO和Mn₂O₃标样的XAS. 原位反应池用于获得样品在常压不同温度下的XAS数据. 原位池是在商业Linkam T95装置(购于Linkam Scientific Instruments Ltd)的基础上进行改进而来. 化学气氛处理的顺序是先充He气, 后充10% H₂-90% He, 最后充10% CO-90% He. 对于一种气体, 升温顺序是从室温到300 °C, 然后退火到室温. 升温速率是5 °C/min, 到了目标温度点, 采谱之前需保温1 h. XAS数据利用Ifeffit软件包处理^[34]. 数据处理使用 k^2 加权, 用FEFF(6.0版本)计算散射振幅和相移^[32]. 由拟合MnO和Rh箔标样得到的振幅衰减因子(S_0^2)分别为0.65和0.85. 通过分析可以计算得到结构参数, 例如配位数(N)、键长(R)、Debye-Waller因子(σ^2)和内势能移动(ΔE_0).

3. 结果与讨论

样品的详细TEM表征详见文献^[19]. 这里, TEM仅用来确认Rh-Mn纳米粒子负载在碳纳米管内壁. Rh-Mn@CNT催化剂的TEM照片见图1, Rh-Mn颗粒以约2 nm的粒径分散在碳纳米管道内.

实际催化反应一般发生在特定的温度和气氛下. 为

了研究Mn和Rh的真实化学态和局域几何结构, 我们对其进行了不同气氛和不同温度下的原位XAS表征. XAS测量前, 样品放置在空气中不作其它任何处理. 样品的典型Mn K边XAS数据见图2(a). 需要注意的是在7100 eV能量附近存在一个小跳跃, 暗示着存在Fe杂质. 进一步的Fe K边XANES数据显示其谱形与 Fe_2O_3 存在相似, 揭示了Fe杂质是以氧化物形式存在. 这些微量的Fe杂质可能来源于碳纳米管的制备过程. 为了排除Fe元素的信号干扰, 我们选择7050 eV作为Mn K边EXAFS采集的能量上限.

为了更好地理解 H_2 气氛对Rh-Mn纳米粒子结构的影响, 需要检查颗粒在惰性气体中的稳定性, 也需要去除吸附在颗粒表面的小分子(例如水分子). 因此, 我们进行了He气氛下的XAS测量, 不同温度下He气氛中的Mn K边XANES谱见图3(a). 在6540.7 eV处存在一个边前峰, 暗示着大多数的Mn以Mn氧化物形式存在. 很有意义的是, 这些XANES谱都存在很宽的主边区, 表明存在混合Mn氧化物(MnO_x). 此外, 这些不同温度下的XANES谱都比较接近, 说明这些混合Mn氧化物在He气氛下相对稳定. 当温度升高时, 吸收边位置向低能端有微小的移动, 这主要归结于Mn氧化物的部分还原. 相应的EXAFS数据的FT谱见图3(b). 这些谱表现出相似性, 表明Mn的局域结构没有发生明显变化. 2.7 Å处的峰可以归结于Mn-O-Mn路径的贡献. 且其峰强度很弱, 表明 MnO_x 是无序结构主导的. 这些FT谱没有明确的物理意义, 不可能用一个简单的结构模型来描述.

在He中热处理后, 样品进一步在不同温度下的10% H_2 -90% He气氛中处理. Mn K边XANES见图4(a). 随着温度升高, 低宽的主边区边变得高瘦, 且吸收边位置向低能端有小的移动, 表明发生了还原, 混合Mn氧化物趋近于一纯相. 对应的Mn K边EXAFS的FT谱见图4(b), 在~1.7和~2.7 Å处的峰分别归结于Mn-O和Mn-O-Mn的贡献. 当温度达到和超过250 °C时, 样品的EXAFS谱表现出与MnO相似的特征, 主要体现在在1.7, 2.7, 4.8和5.8 Å附近存在有意义的峰, 表明在这些阶段大多数Mn以MnO形成存在. 尽管通过Mn K边的位置很难确定Mn的化学态^[35], 但是Mn的K边位置与简单的Mn氧化物(例如MnO, Mn_3O_4 , Mn_2O_3 和 $\beta\text{-MnO}_2$)之间存在一种近似线性的关系^[36,37]. 因此通过与标样对比, 可以确定比较接近的Mn物种的氧化态^[38]. 200 °C退化的样品、MnO及 Mn_2O_3 的XANES谱和相应的 k 空间EXAFS振荡见图4. 这些结果显示助剂Mn的化学态接近+2价. 这一结果与

广泛接受的观点即MnO很难被还原成金属Mn相吻合^[30,39]. 根据EXAFS数据, 没有发现明显的Mn-O-Rh和Mn-Rh的贡献, 暗示着Mn和Rh之间不存在强相互作用.

在不同气氛和温度下的Rh K边XANES数据见图5(a). 主边区中心在23240 eV附近的峰来源于1s电子到未占据的 p 轨道的跃迁^[40]. 因此, 与氧化态相关的任何变化都会反映在这个吸收峰上. 图5(a)表明室温和150 °C下样品的Rh K边位置都接近于 Rh_2O_3 的, 揭示其中的Rh以 RhO_x 存在. 而当温度达到250 °C时, 吸收边位置移动到接近Rh箔位置, 说明形成了金属Rh. 同时, 也说明不存在由Mn引起的显著的电子效应, 这一结果与Schwartz等^[28]的结果相似. 图5(a)说明这些氧化的Rh粒子不稳定, 当温度达到250 °C时在He气氛下就会分解成金属Rh粒子. H_2 -TPR结果也发现 Rh_2O_3 不稳定, 在 H_2 气氛中大约150 °C就会被还原^[41,42]. 相应的Rh K边EXAFS数据见图5(b). 位于1.5 Å和2.5 Å附近的峰归属于Rh-O和Rh-Rh路径的贡献. 也未发现Rh-Mn的贡献, 暗示着没有形成Rh-Mn双金属合金.

He气处理过后, 样品紧接着按顺序在10% H_2 -90% He及10% CO -90% He气氛中热处理. 在这两种气氛下的Rh K边XANES见图6. 图中显示所有的XANES基本上相同, 说明Rh的化学态没有变化, 均为金属Rh. 相比之下, EXAFS的FT谱峰的强度与温度有关(图7), 整体趋势是随着温度升高, Rh-Rh配位峰的强度下降, 说明Rh结构的无序度和Rh的分散性有一定程度的提高.

通过拟合Mn K边和Rh K边EXAFS数据所获得的参数见表1. 数据显示, Rh-Mn@CNT样品经过还原后(AN_200)的Mn-O和Mn-O-Mn键长与MnO标样的非常接近, 而且, 其Mn-O的配位数(5.3 ± 0.5)接近于MnO的, 说明AN_200样品中的Mn大多数与O结合. 此外, 其Mn-O-Mn壳层的配位数(8.5 ± 1.5)明显低于MnO的, 暗示MnO颗粒的尺寸非常小. 还原前的Rh-Mn@CNT样品(RT_He)具有与 Rh_2O_3 相近的Rh-O和Rh-O-Rh键长, 但其Rh-O-Rh配位数(1.4 ± 0.6)明显小于 Rh_2O_3 的, 说明RT_He样品中的Rh以 Rh_2O_3 团簇形式存在. 对于还原后的Rh-Mn@CNT样品(RT_ H_2), 其Rh-Rh配位数(5.3 ± 0.8)明显小于Rh箔的, 说明金属Rh在催化剂上是高分散的. 根据Rh等的团簇模型^[43,44], 估算得出Rh粒子的平均尺寸小于1 nm. 结合前文的TEM结果, 也可以估测出MnO颗粒的尺寸是1–2 nm.

总之, 对于还原后的Rh-Mn@CNT催化剂, 通过XAS分析没有观察到Mn-Rh和Mn-O-Rh的贡献, 说明MnO颗

粒与Rh团簇之间尽管存在物理接触但是不存在强烈的化学相互作用, 而且在温度从250 °C升高到300 °C过程中, MnO颗粒的尺寸发生变大的同时Rh团簇的尺寸则变小, 暗示金属Rh团簇在MnO颗粒上的分散性提高. 因此, 可以推测出助剂Mn的存在主要是提高了Rh的分散性.

4. 结论

利用XANES和EXAFS技术研究了限域在碳纳米管内的Rh-Mn纳米粒子的结构. Rh-Mn粒子以约2 nm的均一尺寸分布在碳纳米管道内. 还原前, 样品中的Mn和Rh分别以MnO_x和Rh₂O₃团簇形式存在于Rh-Mn粒子中. 在

还原气氛下, MnO_x被还原成稳定的MnO. 相比较而言, Rh₂O₃团簇不稳定, 在He气氛下250 °C就会发生分解形成Rh团簇. 形成的Rh团簇在还原气氛下相对比较稳定而保持金属态. Rh与Mn之间不存在明显的相互作用.

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