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Influence of oxidation on heat-treated activated carbon support properties and metallic dispersion of Ru/C catalyst

Hong Zhu, Wenfeng Han, and Huazhang Liu*

Institute of Catalysis of Zhejiang University of Technology, State Key Laboratory of Green-chemistry Synthesis Technology, Hang Zhou 310014, P R China

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Heat-treated activated carbon has been oxidized to improve the properties related to the use as a support for the preparation of 5wt% Ru/C catalysts by impregnation. The pore structure, surface oxygen groups of the heat-treated activated carbon before and after oxidation in the gas and liquid phase, as well as catalytic activities and dispersion of Ru in the catalysts were investigated systematically. The pore structures of the samples were characterized by N_2 physisorption. Temperature-programmed desorption (TPD) was conducted to determine the chemical properties of the samples. Ru dispersion was measured by CO pulse chemisorption. The effects of oxidation treatments on carbon surface chemistry and pore structure which are closely related to Ru dispersion and catalytic activity, was examined. Furthermore, the modified heat-treated activated carbon support obtained by gas phase oxidation in CO_2 and liquid phase oxidation in nitric acid was more suitable to prepare Ru-based catalysts for ammonia synthesis than that without treatment.

KEY WORDS: ammonia synthesis; Ru dispersion; surface oxygen groups; heat-treated activated carbon.

1. Introduction

Ru-based catalyst as a second-generation catalyst for ammonia synthesis is very attractive to researchers in both industry and academia. It has been reported that some forms of activated carbon, when subjected to special treatments, could yield active Ru catalysts [1,2]. Such supports together with proper Ru promotion, has allowed development of the commercial non-Fe ammonia synthesis process [3–7]. However, methenation of carbon remains a key point in the high pressure production of a Ru/C catalyst. In order to improve support resistance, some methods of pretreatment at high temperature were studied. The higher the temperature of the heat treatment, the higher is the stability of the support, but the surface area is decreased markedly [8,9]. Therefore, oxidation treatments are expected to improve surface area, porosity and hydrophobicity of heat-treated activated carbon.

Because the physical and surface chemical properties of the carbon are alterable, the surface chemistry of such supports has been studied widely [10–13]. It is well known that the nature of the functional groups on the carbon surface can affect the physical and chemical characteristics of a catalyst. They may be modified by suitable thermal or chemical post-treatments. Oxidation in the gas or liquid phase can be used to increase the concentration of surface oxygen groups [14,15]. However, there are few reports in the literature about Ru catalysts on heat-treated activated carbon for the synthesis of ammonia.

In this work, the relationship between the chemical nature of the oxidation-modified graphitized carbon surface, the dispersion of the metallic catalyst and its catalytic properties were studied systemically. The studies were focused on a Ru catalyst on heat-treated activated carbon supports with different oxidation treatments for the synthesis of ammonia.

2. Experimental

2.1. Treatment of activated carbon

A commercial coconut shell-derived activated carbon (denoted as AC, obtained from Hainan Carbon Ltd.) was used as the starting material. Some of this carbon was used without any treatment. The remainder was divided into several portions, and thermally and/or chemically modified in different ways:

(i) AC was heated at 1900 °C for 2 h under argon at a pressure of 400 Pa, and is the product was named G.
(ii) G was heated in a stream of 10% O_2, 90% N_2, and the product was named GO.
(iii) G was heated in a stream of CO_2 at designated temperature, and the product was named GC.
(iv) GO and GC were oxidized with nitric acid at boiling temperature, followed by filtration, washing with

*To whom correspondence should be addressed.
E-mail: cuihua@zju.edu.cn

distilled water and drying at 110 °C for 24 h, the products were named GON and GCN, respectively.

2.2. Preparation and activity test of ruthenium catalysts

Supports were impregnated with an aqueous solution of ruthenium chloride for 12 h, the nominal Ru loading was 5.0 wt%. After drying in air at 110 °C for 2 h, 2 wt% Ba and 14 wt% K were impregnated in the same way. The precursor was reduced in flowing hydrogen at 450 °C for 10 h.

The ammonia synthesis reaction was carried out in a fixed-bed reactor (diameter 14 mm) with a flowing gas mixture of $H_2 + N_2$ (3:1, v/v) at 400 °C, with a space velocity of 10,000 h^{-1} and a pressure of 10 MPa. The catalyst (1.0–1.4 mm, 2 mL) was loaded in the isothermal zone of the reactor, and both ends of the catalyst bed were filled with silica to prevent the synthesis gas from channeling. The concentration of ammonia in the exit under given conditions was determined by the method of sulfuric acid neutralization. The activity was expressed as NH_3vol%.

2.3. Characterization of carbon supports and ruthenium catalysts

The structure, texture and surface oxygen groups were investigated by N_2 physisorption and He temperature-programmed desorption mass spectrometry (TPD-MS). The ash content was determined by heating in air at 800 °C to constant weight.

The surface functional groups were determined by TPD-MS, which was performed on a Micromeritics AutoChem 2910 attached to a QMS 200 (Omnistar) mass spectrometer. A 50 mg sample was heated to 50 °C and held at that temperature for 1 h in flowing helium to remove absorbed water and other impurities on the surface of the sample. After cooling to room temperature, the sample was heated to 1000 °C at a heating rate of 10 deg C/min in He at a flow-rate of 40 mL/min. The evolution of CO and CO_2 from the decomposition of the surface groups was monitored by mass spectrometry.

The dispersion of Ru was measured by CO pulse chemisorption. Pulse chemisorption was done with a Micromeritics AutoChem 2910. The active loop gas was pure CO (>99.99%). The stoichiometry factor for CO chemisorption was 1. Before the experiment, the sample was reduced in a H_2 flow at 450 °C for 2 h, and then purged with a He flow for 1.5 h at the same temperature. When the sample was cooled to 30 °C in He, CO was pulsed into the sample until no CO was adsorbed.

N_2 adsorption/desorption isotherms of the samples at the temperature of liquid nitrogen were obtained with a Micromeritics ASAP2010. Before each analysis, the samples were outgassed at 300 °C and 10^{-5} torr for 6 h. The adsorption isotherm data were used to calculate the surface area of each sample via the Brunauer, Emmett and Teller (BET) equation. Total pore volumes were derived from adsorption data at a relative pressure of $P/P_0 = 0.99$ and mesopore volumes were calculated by the t-plot method.

3. Results and Discussion

3.1. Effect of thermal and oxidation treatment on the texture of activated carbon

Table 1 summarizes the specific surface areas (BET_SSA) and pore volumes of the carbon used in this study. According to the literature [16], the mesopore is more important to Ru dispersion than the micropore and mesopore volumes are given in table 1. It can be seen that the original activated carbon (AC) has a huge surface area and a mesopore volume that is about 33%

Table 1
Surface parameters of activated carbon materials

Sample	Treatment conditions			BET_{SSA} ($m^2 \times g^{-1}$)	V_{total} ($cm^3 \times g^{-1}$) ($P/P_0 = 0.99$)	V_{meso} ($cm^3 \times g^{-1}$)	Ash content (%)	Weight loss during oxidation (wt%)
	Temperature (°C)	Time(h)	Oxidizing agent					
AC	–	–	–	1023	0.55	0.18	2.9	–
G	1900	2	–	355	0.19	0.07	1.8	–
GO1	400	16	O_2+N_2	591	0.29	0.06	1.1	28.5
GO2	450	16	$O_2 + N_2$	891	0.41	0.07	1.0	33.9
GO3	500	16	$O_2 + N_2$	756	0.36	0.06	1.0	36.1
GO4	450	12	$O_2 + N_2$	681	0.30	0.05	1.1	32.2
GO5	450	20	$O_2 + N_2$	796	0.30	0.05	1.1	35.4
GC1	800	6	CO_2	673	0.39	0.15	1.0	23.6
GC2	850	6	CO_2	1129	0.64	0.20	1.0	25.8
GC3	900	6	CO_2	893	0.51	0.17	1.0	32.2
GC4	850	9	CO_2	902	0.60	0.16	1.0	29.3
GC5	850	3	CO_2	606	0.37	0.20	1.0	23.4
GON	GO2 treated with HNO_3 for 5 h			878	0.42	0.06	0.9	–
GCN	GC2 treated with HNO_3 for 5 h			1085	0.64	0.20	0.8	–

of the total pore volume. After heat-treating at 1900 °C for 2 h, the surface area was decreased greatly (sample G), and its pore structure was destroyed. Oxidation by a mixture of O_2 and N_2, or CO_2 and nitric acid are expected. to restore the surface area and pore structure.

After oxidation in 10% O_2, 90% N_2, or in CO_2, the surface areas and porosities of heat-treated activated carbon preparations are recovered, at least in part. Table 1 show that the oxidation conditions are important for increase of the surface area and pore volume of the samples. For 10% O_2, 90% N_2, oxidation at 450 °C for 16 h is the most effective condition; about 90% of the surface area and pore volume are restored. The weight loss during oxidation was 33.9%. However, greater porosity is achieved by oxidation in CO_2. There is a correlation between oxidation conditions and pore structure. Suitable conditions for the oxidation treatment depend on the treatment time, the temperature and the oxidizer reagent. Longer and more severe oxidation leads to a sudden destruction of the physical structure of the activated carbon, which may be a result of the destruction of some of the thin porous walls being oxidized in excess. For instance, after oxidation at 500 °C in 10% O_2, 90% N_2 for 16 h, weight loss was as high as 36.1%. By contrast, a lower temperature and a shorter time are not efficient at fully recovering the original surface area and porosity. Oxidation at 850 °C for 6 h in CO_2 (GC2) yielded the largest surface area (1129 $m^2 \times g^{-1}$)and pore volume (0.64 $cm^3 \times g^{-1}$), especially the mesopore volume (0.20 $cm^3 \times g^{-1}$), among the samples investigated. Furthermore, the ash content is as low as 1.0%.

Small but noticeable decreases in surface areas and pore volumes were observed for the HNO_3-treated samples. However, ash content decreased continuously to 0.8% after treatment with HNO_3.

3.2. *Effect of carbon pretreatment on the surface oxygen groups*

It is well known that the surface oxygen groups of the carbon support play a major role in determining the extent and strength of interaction between the metal precursor and the support during preparation of the catalyst. TPD experiments can provide more information about the amount and nature of oxygen surface groups. During thermal desorption, the groups desorb primarily as CO and CO_2 at different temperatures.

Figure 1 shows the CO and CO_2evolution profiles obtained with carbon supports AC, G, GO2, GON, GC2 and GCN. It can be seen that the raw carbon, AC, contains a small amount of acid groups (mainly carboxylic or lactonic) evolving as CO_2 at low temperature (< 400 °C), and relatively greater amounts of neutral or weak acidic groups (mainly carbonyl and phenolic) evolving as CO at temperatures higher than 500 °C. However, sample G has no noticeable CO or CO_2evolved on the whole. As expected, oxidation of heat-treated activated carbon, either with oxidizing gas (10% O_2, 90% N_2 or CO_2) or HNO_3 leads to a noticeable increase of surface oxygen groups.

As shown in figure 1, after oxidation in CO_2 (GC2), a few carboxylic acid lactonic groups, and carbonyl oxygen surface groups are introduced according to the CO and CO_2 profiles, respectively [17–22]. After oxidation in 10% O_2, 90% N_2 (GO2) a greater amount of carboxylic or lactonic acid groups and carbonyl groups are produced. Noticeably, GCN and GON, which are GC2 and GO2 treated with HNO_3, respectively, have many more groups. For sample, GCN has the greatest CO evolution peak at temperatures above 700 °C among the samples investigated. GON has the largest CO_2 evolution peak compared with the other samples. So, after treatment with HNO_3, lots of carboxyl, carboxylic anhydride and/or lactonic groups whose decomposition temperatures are 200–400 and 400–700 °C, respectively, are introduced into the CO_2 evolution profiles, and numerous phenolic, quinone and carbonyl groups are possessed by GON, whose decomposition temperatures are between 600 °C and 900°C in the CO evolution profiles [23].

Figure 1 show clearly that GCN and GON have more total surface groups as a whole than GC2 and GO2, respectively. With these extra acid groups, they can provide more deposition sites for the ruthenium

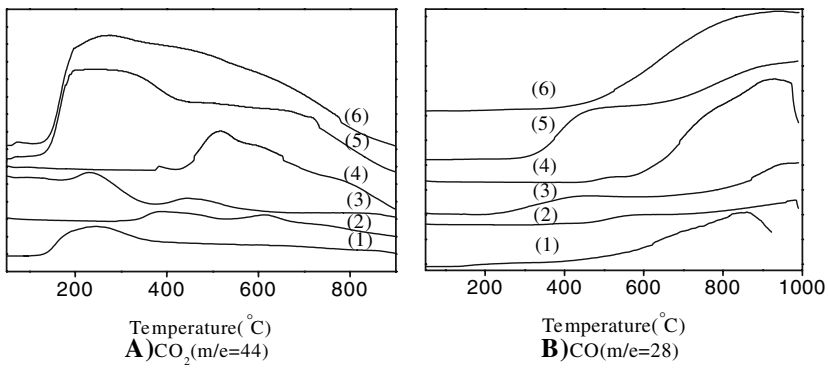

Figure 1. He-TPD-MS profiles of different activated carbons (1) AC, (2) G, (3) GC2, (4) GCN, (5) GO2, (6) GON.

precursor during preparation of the catalyst. Therefore, the hydrophilicity of GCN and GON may be improved.

3.3. Effect of carbon pretreatment on the dispersion of ruthenium

Table 2 presents the results of CO chemisorption and Ru dispersion of 5 wt% Ru/C catalysts. As can be seen, using the thermally treated carbon (G) as support, the catalyst gives quite a low Ru dispersion (2.58%). After oxidizing treatment in 10% O_2, 90% N_2, using GO2 as the support, the Ru dispersion of the catalyst reaches 21.05%. After oxidizing treatment in CO_2, using GC2 as the support, the Ru dispersion is as high as 31.02%. Since the pore walls of the mesopores are the best places for the metallic species to reside, it can be concluded that oxidation in CO_2 can improve the physical characteristics of the carbon support by increasing metal dispersion more than oxidation in 10% O_2, 90% N_2 by observing the change of GO2 and GC2 in V_meso. Although the surface area and mesopore volume of AC are almost the same as those of GC2, the dispersion of Ru on AC is much lower than it is on GC2, which may result from the higher ash content and fewer surface groups of AC.

For the catalyst using GON as the support, the Ru dispersion was 35.84% and the average Ru particle size was 3.76 nm. However, for the catalyst using GCN as the support, the Ru dispersion was 60.04% and the average Ru particle sizes was 2.24 nm. Although GON treated in 10% O_2, 90% N_2 and nitric acid has more surface groups, the corresponding catalysts does not give a high dispersion of Ru, because it was difficult to have adequate mesopores after this treatment. Furthermore, GON has a lot of weak stable acid groups, and they are easy to decompose upon activation of the catalyst, and this will decrease the Ru dispersion. Compared with GO2, it should be noted that the increase in Ru dispersion of GON may be contributed by modified surface groups, especially thermostable acid surface groups, resulting from treatment with nitric acid. The surface oxygen groups play a major role during preparation of the catalyst. The Ru dispersion increase of GCN is more than that of GC2, which helps in elucidating the effect of treatment with nitric acid, by observing the change of the two carbon supports with regard to surface oxygen groups and porosity.

The results show that the Ru dispersion of a carbon-supported Ru catalyst is related closely to the carbon texture. Clearly, a high surface area and a well-developed porosity are essential conditions for achieving large metal dispersions, which usually result in high catalytic activity. However, Ru dispersion is also related closely to the carbon thermostable surface oxygen groups. Prado-Burguete *et al.* [24,25] found that the oxygen surface groups of the carbon support played a major role in the final metal dispersion. When the support is hydrophobic, like heat-treated activated carbon, surface complexes contribute to improve its wettability, and thus make impregnation with polar solvents easier. So, the increase of the thermostable surface groups could improve the hydrophilicity and the dispersion of Ru.

3.4. Activity of carbon-supported Ru catalysts for synthesis of ammonia

Figure 2 presents the ammonia synthesis activities of Ba + K-promoted Ru catalysts on different kinds of carbon support. The unpromoted Ru/C catalysts show almost no activity, due to the electron-withdrawing effect of activated carbon [26, 27]. Therefore, it is not included in figure 2.

The catalyst supported on the original carbon without oxidation treatment shows moderate activity, with the concentration of NH_3 in the effluent at about 10% under the reaction conditions, although the surface area and the pore volume are almost the highest among these kinds of carbon supports. Because the impurity species withdraw electrons from Ru and the promoter, its activity is not as high as expected. Moreover, Ru particles located in the carbon support are easy to sinter under the conditions of the ammonia synthesis reaction. Therefore, the catalysts prepared on the original AC supports are unstable under the high temperature and high pressure, and cannot be considered for practical purposes.

It can be seen that the catalyst supported on G thermally treated carbon, shows a very low level of activity, with the concentration of ammonia in the effluent being less than 3.0%, which is due to the low Ru dispersion. Because of the low specific surface area and the small pore volume of the support in this system, the

Table 2
CO chemisorption and Ru dispersion of 5 wt% Ru/C catalysts

Unpromoted catalyst	CO uptake($cm^3 \times g^{-1}$ STP)	Ru dispersion(%)	Ru surface area ($m^2 \times g^{-1}$ metal)	Ru size (nm)
AC	2.10	23.66	86.45	5.69
G	0.23	2.58	9.43	52.15
GO2	1.87	21.05	76.91	6.39
GON	3.18	35.84	130.92	3.76
GC2	2.75	31.02	113.31	4.34
GCN	5.33	60.04	219.34	2.24

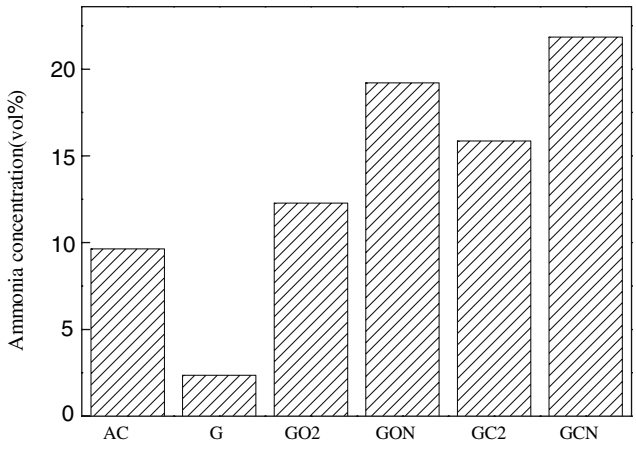

Figure 2. Activities of Ba + K-promoted carbon supported Ru catalysts for ammonia synthesis. (Activity measurement condition: T = 400 °C, $p = 10$ Mpa, GHSV = 10000h^{-1}).

active phase of the catalyst is not utilized sufficiently, even though the resistance of the thermally treated carbon support to methenation is improved under the reaction conditions used in this study.

By contrast, when gas and acid oxidation treatment were introduced, the supports were shown to be more effective. Because of the elimination of contaminating species and improvement of the physical and chemical characteristics, the activities of catalysts supported on modified heat-treated activated carbon are bound to increase. It is found that the order of activity of the ammonia synthesis reaction is GCN > GON > GC2 > GO2. The same sequence is observed for the catalyst Ru dispersion, but not for the mesopore volume of these supports or the amounts of CO_2 and CO evolving during TPD experiments. The catalyst dispersion and catalytic activity are related closely to the surface chemistry and porous structure, which are modified by oxidation and varied by treatment with acid. For example, the optimal support among the above was GCN. One reason is that the surface area and pore volume of GCN was more suitable than those of GO2 and GON, although GCN does not have the greatest amount of surface groups. Another reason is that the surface thermostable oxygen groups of GCN were larger than those of GC2, although they have similar porosity, which improved Ru dispersion. In fact, a sufficient mesopore volume is an essential condition for Ru to reside; and sufficient thermostable acid groups provide effective conditions to improve Ru dispersion and catalytic activity.

4. Conclusions

This investigation has shown the effects of oxidation in the gas or liquid phase on the physical and chemical properties of heat-treated activated carbon supports, Ru dispersion and activity of the catalysts. The following conclusions can be drawn from the data presented here.

(i) Oxidation of heat-treated activated carbon in the gas phase (both 10% O_2, 90% $N_2$and CO_2) can largely recover the original surface area and porosity. Heat-treated activated carbon oxidized in CO_2 has a higher mesopore volume than that oxidized in 10% O_2, 90% N_2. Therefore, suitable conditions for the oxidation treatment depend on the treatment time and temperature, and the identity of the oxidizer reagent.

(ii) Oxygen-containing surface groups can be introduced in significant amounts by oxidation of heat-treated activated carbon both in the gas phase and in the liquid phase. These treatments enhance the wettability of the support and make the surface more amenable to metal dispersion.

(iii) The gas phase oxidation of heat-treated activated carbon in CO_2 increases mainly the surface area and the mesopore volume. Further modification with nitric acid increases especially the concentration of surface groups and decreases the ash content. The support obtained in this way is suitable for the preparation of Ru-based ammonia synthesis catalysts, which have high Ru dispersion and activity.

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