Articles

A Comparative Study of N₂O Conversion to N₂ over Co/AC and Cu/AC Catalysts

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Catalytic conversion of N₂O to N₂ over Cu- and Co-impregnated activated carbon catalysts (Cu/AC and Co/AC) was investigated. Catalytic activity measurements were carried out in a fixed-bed flow reactor at atmospheric pressure. The catalysts were characterized by N₂ adsorption, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). This study aimed to provide insights into the following aspects: the metal dispersion, changes in pore structure, influence of catalyst loading on reaction, and reaction mechanism. Increasing loading of Co or Cu led to decreasing dispersion, but 20 wt % loading was an upper limit for optimal activities in both cases, with too high loading causing sintering of metal. Co exhibited a relatively better dispersion than Cu. Impregnation of metal led to a large decrease in surface area and pore volume, especially for 30 wt % of loading. 20 wt % of loading has proved to be the optimum for both Cu and Co, which shows the highest activity. Both N₂O–Co/AC and –Cu/AC reactions are based upon a redox mechanism, but the former is limited by the oxygen transfer from catalysts to carbon, while N₂O chemisorption on the surface of Cu catalyst controls the latter. The removal of oxygen from cobalt promotes the activity of Co/AC, but it is beneficial for Cu/AC to keep plenty of oxygen to maintain the intermediate oxidation of copper–Cu¹⁺. The different nature of the two catalysts and their catalytic reaction mechanisms are closely related to their different electronegativities.

Introduction

Nitrous oxide (N₂O) has received growing attention during the past decade since it is a contributor to the destruction of ozone in the stratosphere and is recognized as a potent greenhouse gas.¹ Anthropogenic activities have caused continuous N₂O increase in the

atmosphere.^{2–3} The identified anthropogenic sources include adipic acid production for Nylon 66, nitric acid manufacture, fossil-fuel and biomass combustion, and land cultivation.^{4–7} Studies of catalytic decomposition of N₂O have progressed rapidly in recent years. Cata-

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lysts tried for N_2O heterogeneous decomposition include (i) metals such as Pt or Au, (ii) pure oxides (CuO , Co_3O_4 , etc.), and (iii) mixed oxides (perovskite types, ex-hydratalcites). The supports can be alumina, silica, or zirconia; zeolites as catalyst supports have also attracted more and more attention recently.^{5,8}

Activated carbon is a very common and effective support as well as a reductant. In contrast to inorganic carriers, it has a number of advantages. First, the active components are relatively facile to recover, which is important to precious metals. The second advantage is the favorable surface characteristics, which provides the possibility for the catalytic activity enhancement. Third, its highly porous structure is helpful to disperse the metal active phase.⁹ The N_2O –carbon reaction has been studied extensively.^{10–13} However, little work has been reported on N_2O catalytic conversion by using activated carbon as a support at low temperatures. Cu and Co have proved to have strong catalytic effects on NO reduction with carbon.^{14–17} N_2O has been known to be an intermediate of the NO–carbon reaction,^{13,14,18–23} and a preliminary study²⁴ showed that N_2O conversion to N_2 over activated carbon can also be effectively catalyzed by Cu and Co. This paper presents a comparative study of N_2O conversion to N_2 over Cu/AC and Co/AC below 400 °C.

Experimental Section

The catalysts were prepared by impregnating the activated carbon (Calgon, BPL, ground into small particles of 0.4–0.85 mm) with an aqueous solution of Cu nitrate (BDH chemicals, AR grade) or Co nitrate (Ajax chemicals, AR grade) at room temperature for 24 h. The samples were dried at ca. 100 °C overnight and then pretreated at 300 °C in He for 60 min. The reason for the pretreatment at 300 °C is that the samples dried at 100 °C still contained a large amount of water. Meanwhile, as will be detailed, before N_2O reactions or XRD measurements, the samples were subjected to a heat treatment at 500 °C, during which the reaction between $\text{Co}(\text{NO}_3)_2$ (or $\text{Cu}(\text{NO}_3)_2$) and the support could consume a large quantity of carbon. The pretreatment in He at 300 °C is very useful for obtaining a desired amount of sample in our experiments. The activated carbon catalysts prepared with Cu loading of 5, 10, 20, and 30 wt % are designated Cu5/AC, Cu10/AC, Cu20/AC, and

Cu30/AC, respectively; similarly, the activated carbon catalysts with Co loading of 5, 10, 20, and 30 wt % are Co5/AC, Co10/AC, Co20/AC, and Co30/AC, respectively. Generally, catalysts loaded with Cu are referred to as Cu/AC, catalysts with Co as Co/AC, and the parent activated carbon without any Cu or Co as AC.

The N_2O –carbon reaction was carried out under atmospheric pressure in a fixed-bed flow reactor (10 mm inside diameter; 200 mg sample), and the gaseous products were analyzed by using a gas chromatograph (Shimadzu GC-17A) equipped with a thermal conductivity detector and a Carbo-sphere column. The feed gas, with a gas hourly space velocity (GHSV) = 22500 $\text{mL g}^{-1} \text{h}^{-1}$, contained 3000 ppm N_2O in He. Two modes of experiments were employed: (i) temperature-programmed reaction (TPR): heating the fresh samples at 4 °C/min to 500 °C in a $\text{N}_2\text{O}/\text{He}$ mixture; and (ii) isothermal reaction at 350 °C, 380 °C for ca. 150 min. In both cases, the sample was first subjected to an in situ heat treatment in He at 25 °C/min to 500 °C and kept there for 60 min. In case (i) when the temperature was lowered to ca. 30 °C, the reactant mixture was introduced and then the TPR experiment followed. In case (ii) the temperature was lowered to a designated level and the isothermal experiment was initiated by switching He to a $\text{N}_2\text{O}/\text{He}$ mixture.

The N_2 adsorption/desorption isotherms at –196 °C were obtained using a gas sorption analyzer (Quantachrome, NOVA 1200). Samples were degassed for 3 h at 300 °C prior to the adsorption analysis. The BET surface area and total pore volume were obtained from the adsorption isotherms. The t -plot method was used to calculate the micropore surface area and micropore volume.

XRD patterns were obtained with a Philips PW 1840 powder diffractometer. Cobalt $K\alpha$ radiation was employed covering 2 θ between 2° and 90°. The mean crystallite diameters were estimated by the Scherrer equation.²⁵ All samples were subjected to a heat treatment in He at 500 °C followed by a quick cooling to room temperature under a He atmosphere before XRD measurements unless otherwise stated.

Thermogravimetric (TGA) experiments were carried out in a thermobalance (Shimadzu TGA-50). Samples were loaded into a platinum pan and heated under a pure He atmosphere from ambient temperature to 110 °C and held there for 20 min, and then heated to 800 °C with a heating rate of 10 °C/min. For O_2 adsorption, the samples were heated to 500 °C and kept there for 60 min, followed by cooling to room temperature and switching He to 20% O_2/He until a constant weight was reached.

Results and Discussion

Characterization of Samples. Figure 1 presents the results of O_2 adsorption with O_2 adsorption on the blank AC subtracted. It is seen that, in both cases, the amount of O_2 chemisorption increased with increasing metal loading from 5 to 20 wt %. However, a further increase in metal loadings up to 30 wt % led to a significant reduction in O_2 chemisorption indicative of reduction in the active surface areas of the catalysts. Another important phenomenon is that Co possesses a much larger capacity for O_2 chemisorption than Cu at the same metal content.

Figure 2 shows the TGA weight loss curves obtained under He for Co20/AC and Cu20/AC at a constant heating rate. Co20/AC shows a broad low-temperature peak between 150 and 250 °C, and a sharp high-temperature peak centered around 550 °C. This result is in good agreement with the report of Grandia and

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Figure 1. O₂ chemisorption over Co/AC and Cu/AC at room temperature after 500 °C heat treatment in He.

Figure 2. Thermal decomposition rate of Co20/AC and Cu20/AC in He.

co-workers.²⁶ The former peak indicates the cobalt nitrate decomposition to cobalt oxides and the latter represents the cobalt oxide reduction to metallic cobalt or lower valence cobalt oxides. Cu20/AC shows double low-temperature peaks between 150 and 300 °C, and a weak high-temperature peak at ca. 425 °C. According to the XRD results of Marquez-Alvarez and co-workers,¹⁶ a heat treatment at 300 °C in He could not only decompose Cu(NO₃)₂ to CuO, but also could reduce some CuO to Cu₂O (no metallic Cu found). Therefore, the low-temperature peak from 150 to 300 °C should be attributed to the decomposition of Cu(NO₃)₂ and the reduction of some CuO to Cu₂O. The high-temperature peak at ca. 425 °C is very weak, indicating the reduction of remaining copper oxide to metallic form or lower valence oxides. This comparison shows that a higher temperature is needed for the reduction of cobalt oxides by carbon than for that of copper oxides, i.e., copper

Table 1. Crystallite Diameters of Metals

samples	diameter (nm)		
	Co	CoO	Co ₃ O ₄
Co5/AC	15.5	10.0	8.34
Co10/AC		13.5	
Co20/AC		12.9	
Co30/AC		18.1	
	Cu	Cu ₂ O	CuO
Cu5/AC	19.4	17.1	14.6
Cu10/AC	21.6	23.4	
Cu20/AC	24.1	26.7	
Cu30/AC	22.6	30.3	

oxides are easier to be reduced. This corresponds to the results in O₂ chemisorption.

Table 1 summarizes the catalyst phases and the catalyst particle sizes detected by XRD. The following observations are made: (i) In both Co5/AC and Co10/AC, only CoO was detected. In Co20/AC, a new phase—metallic Co appeared beside CoO, while, in Co30/AC, metallic Co disappeared and was replaced by a more oxidized species—Co₃O₄. (ii) In catalysts Cu5/AC, Cu10/AC, and Cu20/AC, two phases—Cu metal and Cu₂O—were detected. Similar to the case of Co30/AC, the catalyst phases in Cu30/AC were characterized by the appearance of a more oxidized species—CuO beside Cu and Cu₂O. (iii) For both Co and Cu catalysts, an increasing loading resulted in increasing catalyst particle or decreasing catalyst dispersion. Moreover, the particle sizes of Co catalysts were smaller than those of Cu catalysts with the same catalyst loading, which means that Co catalysts generally have a better dispersion than Cu catalysts under the same preparation conditions.

It is obvious that catalyst reduction by carbon in an inert atmosphere is favored by small catalyst particles and large catalyst/support interfacial area. A more oxidized phase—Co₃O₄ was observed only in Co30/AC and not in the other three Co catalysts as the former one possesses the largest catalyst particle size or the poorest catalyst/carbon contact. The appearance of metallic Co in Co20/AC means that Co oxides can be reduced to Co metal by the as-received carbon after a heat treatment in He at 500 °C. However, Co metal phase only appeared in Co20/AC instead of Co5/AC and Co10/AC despite the fact that the latter two catalysts have relatively smaller particle sizes or better catalyst/carbon contact. The reason for this controversial fact should be related to the reoxidation of reduced catalyst particles, which is favored not only by the affinity of the metal for oxygen but also by the size and shape of the catalyst particles. Previous study showed that passivation treatment with air even at room temperature can oxidize 2 to 7 monolayers of metal nickel,²⁷ and cobalt is about 25 times easier to oxidize than nickel at room temperature.²⁸ So it is reasonable to think that Co metal did appear in Co5/AC and Co10/AC after the 500 °C treatment in He, but all of the produced Co metal was reoxidized into CoO upon the exposure of samples to air before XRD experiments resulting from the rela-

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tively small catalyst particles in these two catalysts. Montes and co-workers²⁷ worked out the monolayers of reoxidized nickel based upon the surface area of nickel catalyst obtained from H₂ chemisorption and the oxygen uptake obtained from temperature-programmed desorption (TPD). Unfortunately, it is impossible here to make a similar quantitative calculation of the monolayers of reoxidized Co metal, because H₂ chemisorption is highly reversible²⁹ over cobalt and there is so far no alternative gas chemisorption appropriate for the measurement of cobalt surface area. At the same time, nickel oxide generally involves a relatively simple phase—NiO,²⁶ while Co oxides include a variety of forms such as CoO, Co₃O₄, and Co₂O₃, so it is very hard (or nearly impossible) to determine the reoxidized cobalt content just on the basis of the oxygen uptake. The results from XRD and O₂ chemisorption above could indicate that 20 wt % of cobalt may be an upper limit of loading as far as dispersion is concerned. The increase in O₂ chemisorption with the increasing metal loading from 5% to 20% means that the available surface of activated carbon would not be fully utilized at a lower loading. But poor catalyst/carbon contact or even aggregation of metal can possibly occur under too high loading up to 30 wt %, resulting in a decrease in O₂ chemisorption and a more oxidized phase-Co₃O₄ in XRD. It should be noted that reoxidation of Cu is negligible in XRD measurements. A similar conclusion is that 20 wt % of Cu may be an upper limit of Cu loading. At 30 wt % of Cu loading, the appearance of a more oxidized phase-CuO and the decrease in O₂ chemisorption indicate the poor Cu/carbon contact or the sintering of Cu. While, 20 wt % of Cu content can avoid possible metal aggregation without the sacrifice of the available support surface. This will be further confirmed by the catalytic activity measurements later.

As has been noted, the dispersion of Co is better than Cu in activated carbon. Both CuO and CoO are important intermediates during the dispersion of Cu and Co catalysts, respectively. CoO crystallites are cubic, with the length of the cell edges being 4.26 Å, much smaller than the size of monoclinic CuO unit cell ($a = 4.684$ Å, $b = 3.425$ Å, $c = 5.129$ Å). It is also noted that cobalt has a much weaker electronegativity³⁰ and thus a much stronger electrostatic attraction to the surface oxygen on carbon than Cu during impregnation. The stronger propensity of cobalt to surface oxygen may also decrease its possibility of agglomeration during reduction (activation). The above three aspects explain the smaller crystallite size as well as better dispersion of Co catalyst in AC.

A quantitative comparison of the textural structure of all samples is given in Table 2. With increasing metal loading, the surface areas and pore volumes of samples decrease greatly. The ratios of micropore volume to total pore volume (V_m/V_t) are reduced by the impregnation of metal to some degree, indicating that the distribution of metal in activated carbon is not completely uniform and more metal has been distributed in micropores than in mesopores. With increasing loading of Co or Cu from 5 to 20 wt %, the values of V_m/V_t are very close and just a little smaller than that in AC, and further increases

Table 2. Specific Surface Area and Pore Volume of Catalysts

sample	S_{BET} (m ² /g)	V_t (cc/g)	V_m (cc/g)	V_m/V_t
AC	1077	0.51	0.41	0.80
Co5AC	981	0.47	0.37	0.79
Co10AC	912	0.43	0.35	0.80
Co20AC	759	0.37	0.29	0.79
Co30AC	614	0.31	0.24	0.76
Cu5/AC	890	0.43	0.34	0.78
Cu10AC	870	0.43	0.33	0.77
Cu20AC	770	0.39	0.30	0.78
Cu30AC	677	0.37	0.26	0.72

in metal loading up to 30 wt % cause an abrupt decrease in V_m/V_t . This means that the distribution for the former three loadings is relatively uniform. Too high loading up to 30 wt % causes the blockage of a large amount of micropores. There are relatively larger values of V_m/V_t over Co/AC than over Cu/AC at the same metal loading. This means that Co has a more uniform distribution in AC than Cu, further confirming the results obtained from the XRD and oxygen chemisorption measurements.

Isothermal Reaction Studies. Isothermal reactions of N₂O with all samples were carried out at 380 °C after 500 °C heat treatment in He for 60 min, to obtain comparable activity data (Figure 3). It is shown that the N₂O conversion over the parent activated carbon is negligible at 380 °C. The impregnation of either Co or Cu can improve the activity of N₂O-carbon reaction substantially, which means that both Co and Cu have significant catalytic activities for the reaction.

We note that Co/AC exhibited a 100% of N₂O conversion at the beginning of the reaction. However, after a period of time the activity went down sharply and then remained at a constant level. The duration of the high activity as well as the final level increased with the increasing catalyst loading from 5 to 20 wt %, while a further increase in loading up to 30 wt % reduced the constant level to even below that of Co10/AC. Catalyst Co20/AC has the duration of high activity and the highest constant level of conversion (being about 88%). Therefore 20 wt % of Co can be considered as the optimum content.

Contrary to that over Co/AC, the activity of Cu/AC was rather low at the beginning before increasing gradually, then reaching a plateau. Sixty percent of N₂O conversion was observed over Cu5/AC, 85% over Cu10/AC, and 97% over Cu20/AC. Cu30/AC showed a little lower conversion than Cu20/AC. Consequently, 20 wt % of Cu can also be regarded as the optimum content.

A comparison of reaction rates between the catalysts supported by activated carbon and those supported by zeolite shows the advantage of AC as a support for N₂O conversion to N₂. The rate at the plateau is 2.55×10^{-3} mol g⁻¹ h⁻¹ over Co20/AC at 380 °C, compared to 1.35×10^{-3} mol g⁻¹ h⁻¹ over Co-ZSM-5 at 400 °C.⁵ The reaction rate is 2.86×10^{-3} mol g⁻¹ h⁻¹ over Cu20/AC at 380 °C, compared to 2.7×10^{-3} mol g⁻¹ h⁻¹ over Cu-ZSM-5 at 400 °C.⁵ It is seen that activated carbon is a better support for Co and Cu than zeolite in N₂O conversion.

In a study of NO-carbon reaction catalyzed by Cu, Ruckenstein et al.¹⁵ also found that 20 wt % of Cu was the optimum content, which led to the highest activity of NO conversion. They did not offer any explanation of why 20 wt % of Cu can be the best loading. On the basis

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Figure 3. Relationship between N₂O conversion and reaction time for N₂O reduction over (a) Co/AC and (b) Cu/AC (experimental conditions: $P = 1.0$ atm, reaction $T = 380$ °C, GHSV = 22500 mL g⁻¹ h⁻¹, N₂O/He = 3000 ppm).

of characterization obtained from XRD, O₂ adsorption, and N₂ adsorption, we found that loading lower than 20% provided less active sites. Too high loading up to 30 wt % brought about the sintering of metal as well as the poor metal/carbon contact, resulting in the reduction in active sites of catalyst. A metal loading of 20 wt % is high enough to make full use of the available carbon surface area, but low enough to avoid the possible sintering of metal. Therefore 20 wt % of Co or Cu presented the best activity and could be regarded as the optimum content. However, this is just a qualitative explanation. In the study of air-carbon gasification catalyzed by Cu, Radovic et al.³¹ carried out a semi-quantitative study by normalizing the reaction rate with the external surface area of crystallites obtained from XRD measurements, finding that the reaction rate was proportional to the calculated external surface area. The

Table 3. Normalized Reaction Rate by O₂ Chemisorbed

samples	normalized reaction rate (μmol N ₂ O/μmol O ₂ .s)	samples	normalized reaction rate (mmol N ₂ O/μmol O ₂ .s)
Co5/AC	6.34×10^{-3}	Cu5/AC	9.40×10^{-3}
Co10/AC	2.19×10^{-3}	Cu10/AC	8.80×10^{-3}
Co20/AC	4.64×10^{-4}	Cu20/AC	8.63×10^{-3}
Co30/AC	5.30×10^{-4}	Cu30/AC	53.3×10^{-3}

loading of Cu in their study was just ca. 2.0 wt %, so a single phase of metal was obtained. However, in this work, the high metal loading complicates the crystal phases. So it is impossible here to make the same semiquantitative investigation as Radovic et al. did. Chemisorption of gas is another effective method to determine the available surface area of a catalyst. Linares-Solano et al.³² made good use of normalization of calcium-catalyzed carbon gasification rate by CO₂ chemisorption. As has been noted, the hydrogen chemisorption is highly reversible over cobalt,²⁹ thus not satisfactory for cobalt surface area measurements. Oxygen chemisorption is more suitable for the determination of Cu surface area than hydrogen chemisorption, because the interactions between H₂ and Cu are very weak.³³ So we tried to normalize the reaction rate with oxygen chemisorbed, and the results are given in Table 3 (the reaction rates were obtained from the stable level at the end of 150-min isothermal reaction at 380 °C). No clear trend is found for the cobalt catalysts, but the normalized reaction rates over Cu/AC catalysts are very close except for Cu30/AC. As will be discussed, the controlling step for the N₂O-Cu/AC reaction is N₂O chemisorption by the external surface of copper catalyst. Therefore the N₂O-Cu/AC reaction rate was well normalized by the surface area obtained from oxygen chemisorption. As for Cu30/AC, the metal sintering or the poor contact between carbon/metal may be the reason it is exceptional. On the other hand, it is the oxygen transfer from the metal to carbon and the reduction of oxidized metal that limits the N₂O-Co/AC reaction. So oxygen chemisorption is not a good way for the normalization of reaction rate. On the basis of the above analysis, it is concluded that at least two conditions need to be satisfied for the normalization of gasification rate by gas chemisorption: (i) The gasification is limited by gas chemisorption on the available surface area of catalyst; (ii) no sintering of catalysts occurs. Considering the optimum activities over Co20/AC and Cu20/AC, the following discussions will concentrate on 20 wt % catalysts supported on AC.

Figure 4a,b presents the evolution of products during the isothermal reactions over Cu20/AC and Co20/AC at 380 °C, respectively. It is seen that the selectivity to N₂ and CO₂ as defined by $[N_2/(N_2 + NO_x)] \times 100\%$ and $[CO_2/(CO_2 + CO)] \times 100\%$, is 100% for both Co20/AC and Cu20/AC even when 100% of N₂O conversion is reached (e.g., no new NO_x and CO are found in the products). Because one N₂O molecule reacting with carbon generates one N₂ and 0.5 CO₂, normally molar N₂ doubles molar CO₂ in the products if no delay of evolution of oxygen-containing product with respect to N₂ occurs during the reaction. To show more clearly the

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Figure 4. Evolution of products during isothermal N_2O reaction over Co_{20}/AC (a) and Cu_{20}/AC (b) at 380°C .

oxygen balance in the product analysis, the CO_2 concentration is doubled in Figure 4. In this way, N_2 concentration is equal to CO_2 concentration in the products if the evolution of oxygen-containing products is not delayed with respect to N_2 ; otherwise, CO_2 concentration is less than N_2 concentration. An interesting common trend in both cases is that CO_2 evolution is initially delayed with respect to the evolution of N_2 , resulting in a negative oxygen balance. The delay is much larger over Co catalyst than over Cu catalyst. This information will complement the discussion on the reaction mechanism later.

To confirm the different patterns of activities over Co and Cu catalysts, additional isothermal reaction experiments were conducted over Co_{20}/AC and Cu_{20}/AC at a lower temperature, 350°C . Following 150 min reaction at 350°C , heat treatment in H_2 was also carried out by switching 3000 ppm $\text{N}_2\text{O}/\text{He}$ to 1% H_2/He for 30 min. In Figure 5a, the pattern of activity change over Co_{20}/AC at 350°C is found the same as at 380°C except for the relatively shorter time for 100% of N_2O conversion and the lower constant level. After H_2 treatment at 350°C ,

Figure 5. Influence of heat treatment in H_2 on N_2O reaction with Co_{20}/AC (a) and Cu_{20}/AC (b) (reaction $T = 350^\circ\text{C}$, $P = 1$ atm, $\text{GHSV} = 22500 \text{ mL g}^{-1} \text{ h}^{-1}$, $\text{N}_2\text{O}/\text{He} = 3000$ ppm).

$^\circ\text{C}$, the N_2O conversion over Co_{20}/AC increased from ca. 68% to 85%, and then decreased quickly. The 500°C H_2 treatment led to a higher N_2O conversion up to 100%, which lasted for about 10 min, and then decreased rapidly to the same constant level. In Figure 5b, Cu_{20}/AC also presented a lower N_2O conversion initially at 350°C , followed by a gradual increase to ca. 74%. Interestingly, H_2 treatment caused the N_2O conversion to sharply decrease to 30% and then quickly recover to the same plateau level. We can see that catalyst reduction by H_2 and carbon resulted in the same patterns of activity over Co/AC and Cu/AC .

Temperature-Programmed Reaction (TPR) Studies. Temperature-programmed reactions (TPR) were carried out over Co_{20}/AC , Cu_{20}/AC , and the blank activated carbon (Figure 6). No obvious reaction is observed over the activated carbon until ca. 440°C , and the temperature required to reach 100% N_2O conversion (T_{100}) is over 600°C . The impregnation of Co or Cu caused a substantial decrease both in the starting reaction temperature and the T_{100} . At ca. 400°C , 100%

Figure 6. Temperature-programmed reaction over Co20/AC, Cu20/AC, and pure AC (reaction conditions: $P = 1$ atm, GHSV = 22500 mL g⁻¹ h⁻¹, N₂O/He = 3000 ppm).

N₂O conversion is reached in both cases. Another interesting comparison of Co/AC, Cu20/AC, and AC in Figure 5 shows that the starting reaction temperature as well as the T_{100} over Co20/AC is lower than that over Cu20/AC.

The shape of the TPR curves demonstrates that the N₂O-carbon reactions over Cu/AC, Co/AC, and AC can be described as a first-order reaction with respect to N₂O under the given experimental conditions, which is consistent with the results of Smith et al.³⁴ on the N₂O-carbon reaction in a batch reactor. Assuming that the microreactor operation approximates plug flow behavior, the apparent activation energies are calculated to be 111.5 kJ/mol for AC, 80.5 kJ/mol for Cu20/AC, and 63.4 kJ/mol for Co20/AC. A detailed analysis of the evolution of products will be given in the discussion, providing insights into the reaction mechanism.

Discussion

Figure 7 presents the evolution of products during TPR experiments. Over Co20/AC, before 140 °C, no products other than N₂O were observed, and N₂O was a little less than 3000 ppm. Two reasons may account for the weak negative nitrogen balance: the instability of the experiment system at the beginning and adsorption of N₂O on Co20/AC. N₂ was detectable at ca. 140 °C, but the evolution of CO₂ did not start until ca. 190 °C. This was clearly due to the dissociative chemisorption of N₂O over cobalt catalyst. With the emission of CO₂, N₂O conversion began to increase quickly accompanied by a quick increase in N₂. This reveals the importance of oxygen transfer from metal to carbon. However, the evolution of CO₂ was greatly delayed with respect to N₂ even when 100% N₂O conversion was reached, indicating the retention of oxygen on metal Co or lower valence cobalt oxides. Over Cu20/AC, the temperature required for detectable N₂ emission was ca. 200 °C, being much higher than that over Co20/AC. Therefore chemisorption of N₂O over copper catalyst is

Figure 7. Evolution of products during TPR over Co20/AC (a) and Cu20/AC (b).

not as facile as over cobalt. The emission of N₂ was very slow initially and became quick once the evolution of CO₂ started at ca. 250 °C. This was similar to the case over Co20/AC. The delay of CO₂ evolution with respect to N₂ over Cu20/AC was negligible before 400 °C, at which 100% N₂O conversion was reached. This demonstrates the stronger ability of Cu to transfer oxygen to carbon and recover the reduced state compared with that of Co, which has been proved by the easier reduction of Cu oxides in Figure 2. It is also noted that over 400 °C, CO₂ concentration even became higher than N₂ concentration. This may be related to the decomposition of the original oxygen complexes activated by the N₂O atmosphere on the surface of Cu/AC.

Therefore, the mechanism of the N₂O-carbon catalyzed reaction is actually an redox cycle, which is analogous to that of O₂-, CO₂-, H₂O-carbon,³⁵ and NO-carbon catalyzed reaction.^{14,19-23} The reaction is initialized by the N₂O dissociative chemisorption, fol-

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lowed by oxygen transfer from the catalyst to carbon, and ended by the release of carbon–oxygen surface complexes. This explanation is further confirmed by the different patterns of activities over Co/AC and Cu/AC during the isothermal reaction in Figure 3. A very high activity over Co/AC was observed at the onset of the reaction as metallic Co or lower valence Co oxides (resulted from 500 °C treatment in He) can accept oxygen from N₂O reduction more easily and become higher valence Co oxides. However, Co oxides are difficult to be reduced (Figure 2), which limits the whole reaction. As the reaction proceeds, more and more oxygen covered the Co oxides and could not be transferred to the carbon surface to form CO₂ quickly; resulting in deactivation. The activity decreased sharply, until another oxygen balance was built up. This is further evidenced by the large delay of CO₂ evolution with respect to N₂ in the isothermal reaction (Figure 4a), because of the oxygen retention on the surface of oxides not being released in time. A comparison of XRD patterns of Co20/AC before and after reaction with N₂O at 380 °C (Figure 8a) shows that metallic Co was replaced by a more oxidized phase-Co₃O₄ after 150 min isothermal reaction, and the CoO peak became much sharper. This indicates that at the plateau, the N₂O conversion over Co/AC was actually a redox cycle between CoO and Co₃O₄.

As a poor oxygen acceptor, Cu showed a relatively lower activity initially during the isothermal reaction. This indicates that N₂O reaction with Cu/AC is limited by the first step of reaction—N₂O chemisorption. The much shorter delay in CO₂ evolution with respect to N₂ over Cu20/AC (Figure 4b) confirms the stronger ability of oxygen transfer from the metal particle to the carbon surface. A comparison of XRD patterns of Cu20/AC before and after 150 min reaction with N₂O at 380 °C (Figure 8b) shows that most of Cu metal produced during heat treatment was reoxidized into Cu₂O or CuO during the reaction. Considering the asymptotic increase in activities of Cu/AC during the reaction, it is suggested that Cu₂O is more active than Cu metal. The N₂O conversion over Cu/AC at a steady state is a redox cycle between Cu₂O/CuO. Stronger evidences came from H₂ treatment of Cu20/AC (in Figure 5b), which reduced Cu oxides into Cu metal resulting in the abrupt decrease in activity. Therefore, it is necessary to keep plenty of oxygen complexes on copper catalyst in order to maintain the intermediate oxidation-Cu¹⁺. Cu¹⁺ species are regarded as most effective active sites in hydrogenation reactions over Cu catalysts dispersed on carbon³⁶ and mineral support.³⁷ A more relevant study is N₂O decomposition over Cu–ZSM-5 catalyst. It is proposed that the charge donation from the catalyst to N₂O is triggered by excited Cu¹⁺–Cu¹⁺ dimers resulting in a fast decomposition, and the reaction turned out to be proportional to the Cu¹⁺ concentration.³⁸ A study in good agreement with our work is the NO selective reduction by hydrocarbons over Cu–ZSM-5 and Cu/Al₂O₃,³⁹ in which Cu¹⁺ proved to be most active sites, and appearance of Cu⁰ resulted in the reduction of activity.

Figure 8. XRD patterns of Co20/AC (a) and Cu20/AC (b) before and after isothermal reaction with N₂O at 380 °C (*, before reaction; **, after reaction).

Unfortunately, why Cu¹⁺ is more active than Cu⁰ or Cu²⁺ was not dealt with in those studies. A possible explanation may be the participation of the neighboring ions in the M–O–M system. It is rationalized by the so-called Zener double exchange⁴⁰ where two ions, differing by one oxidation state and bonded via an oxygen ion, can exchange an electron through the O 2p orbital. This leads to an average and easily adaptable oxidation, thus facilitating the redox cycle.⁴¹ Therefore, although Cu⁰ may have a stronger ability for N₂O dissociative chemisorption, Cu¹⁺ is more efficient in the redox cycle.

In the study of Illán-Gómez et al. on NO–carbon reaction catalyzed by Co and Cu (with loadings less than 4 wt %),¹⁴ they preheated the catalysts to 900 °C in He before reaction, so pure Co and Cu metals were obtained

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in carbon. They found that the activities were relatively stable at high temperatures and decreased quickly at low temperatures on both Co/AC and Cu/AC. As has been noted, in our experiments, Co/AC presented a higher initial activity for a period of time followed by a quick decrease to a constant level, while the activity over Cu/AC showed a gradual increase until equilibrium. The difference between the activities over Co/AC and Cu/AC were not observed in the study of Illán-Gómez et al.,¹⁴ because of the low loading of catalyst (less than 4%) in their study. Therefore the high loading catalyst in our study provided both improved activity and clearer differences between Co/AC and Cu/AC.

A mechanism of N₂O reduction by pure carbon suggested by Smith et al.,²⁷ which was accepted by most of the researchers, is as follows:

where C(O) is a carbon–oxygen surface complex formed during reaction. N₂O is able to scavenge oxygen atoms from the carbon–oxygen surface complexes formed by its reaction with these sites.⁴² An alternative mechanism is somewhat more elaborate.⁴³

where C_f is a carbon active site produced by the release of carbon–oxygen surface complexes. However, to the best of our knowledge, no report can be found on the detailed analysis of mechanism of N₂O–carbon catalyzed reaction.

According to the above analysis, the basic mechanism of N₂O–carbon in the presence of metal catalyst is the same, except that the catalyst facilitates the oxygen transfer from N₂O to carbon. On the basis of our results and discussions above, the possible mechanism for the high activities of Co and Cu is suggested as follows:

where M denotes a catalyst active site. Equations 8 and 9 represent the dissociative chemisorption of N₂O over catalyst; eqs 10 and 11 represent the diffusion of oxygen from metal (or metal oxides) to the edge carbon sites to form carbon–oxygen surface complexes; eqs 12 shows the release of carbon–oxygen surface complexes. Dissociative chemisorption of N₂O on the catalysts active centers is generally envisaged as a charge donation from the catalyst into the antibonding orbitals of N₂O, destabilizing the N–O bonding and leading to scission. Metal surfaces, oxides with local charge donation properties, and isolated transition metal ions with more than one valency can act as such centers.⁴⁴ Actually, O₂ (and NO) reactions with the catalysts are also based upon the same mechanism.³⁰ As Co has a much lower electronegativity than Cu, gas (including N₂O, O₂, and NO) dissociative chemisorption would occur comparatively more readily for the former.³⁰ This is why Co is facile to accept oxygen (in Figure 1a) and hard to be reduced (Figure 2a). The same cause leads to a high activity initially during the isothermal reaction over Co/AC (in Figure 3a). Moreover, as has been noted, the relatively better dispersion of Co (evidenced by XRD patterns) is also related to the lower electronegativity, thus making the pore structure of Co/AC more uniform. An analogous analysis is applicable to Cu/AC except for the opposite role played by the higher electronegativity. According to the previous discussions, N₂O reaction with Cu/AC is limited by eq 8, and eqs 10 and 11 control the reaction in case of Co/AC. Equation 12 is closely related to eqs 10 and 11, and will be discussed in detail next.

N₂O is an intermediate of NO–carbon,^{13,14,18–23} so it is not surprising that similar behaviors between N₂O– and NO–carbon reactions do exist. NO–carbon catalyzed and un-catalyzed reactions have been studied extensively, but the work of Illán-Gómez and co-workers^{14,18–23} seems the most comprehensive so far. A similar redox mechanism suggested by them is as follows:

where S denotes a surface site. In the uncatalyzed reaction, this is a carbon reactive site. In catalyzed NO reduction, this is a reduced catalytic site. It is noted that the mechanism of Illán-Gómez and co-workers emphasizes two aspects of catalysts: (i) the role of metal as an acceptor of oxygen from the reduction of NO, and (ii) the ability of oxidized metal to transfer oxygen to carbon surface and recover reduced metal. They thought

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that the release of carbon–oxygen surface complexes in the presence of a catalyst is the same ones that characterize well the oxygen–carbon reactions, while the third role of catalyst in prompting the release of carbon–oxygen complexes was ignored. Actually, the second role of catalyst is closely related to the release of carbon–oxygen complexes from the carbon surface as more oxygen atoms in carbon active sites are useful for breaking the neighboring C–C bonds.⁴⁵ This means that a catalyst with a strong ability of oxygen transfer to carbon can also accelerate the release of carbon–oxygen surface complexes. Therefore in our mechanism, we think that C(O) can further accept oxygen from the oxidized metal and become more oxidized carbon–oxygen surface complexes, from which only CO₂ is released. This is evidenced by the 100% CO₂ conversion during both the isothermal reaction and TPR experiments.

Conclusions

Increasing loading of Co or Cu in activated carbon from 5 to 30 wt % resulted in increasing particle size or decreasing dispersion of metal. A loading of more than 20 wt % can possibly lead to catalyst sintering or poor contact between the metal and carbon. The surface area and pore volume of the catalyst decrease greatly due to the impregnation of Co or Cu. The metal distribution is not that uniform and there are more micropores blocked than mesopores, especially at 30 wt % of metal

loading. Co showed a relatively more uniform distribution than Cu in AC.

Activated carbon has proved to be an effective support. Both Cu and Co exhibited high catalytic activities for the N₂O–carbon reaction. Metal loading of 20 wt % was found to be optimum in both cases. During the process of N₂O–carbon reaction, Cu and Co showed different catalytic characteristics. After 500 °C heat treatment in He, Co/AC showed a high activity initially during isothermal reactions, but then decreased to an equilibrium level after a period of time; whereas Cu/AC presented a relatively lower activity at the beginning, and then went up to a steady-state asymptotically. Both N₂O–Co/AC and N₂O–Cu/AC reactions are based upon a redox mechanism, but the former reactions are controlled by oxygen transfer from cobalt catalyst to carbon, while the latter are limited by N₂O chemisorption. The removal of oxygen from cobalt catalyst benefits the activity of Co/AC, but plenty of oxygen is needed by copper catalysts to maintain Cu¹⁺, which is more active than Cu⁰. The different characteristics of catalysts are closely related to the different electronegativities of the metals.

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