

Graphite Nanofibers-A Unique Catalyst Support Media

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ABSTRACT

Conventional heterogeneous catalyst systems consist of a metal phase dispersed on a powdered or pelleted carrier and while these classical designs have provided a satisfactory means of supporting small metal particles there is a need for major innovations in this area. The emergence of new nanofibrous materials with diverse structures affords one with the opportunity of supporting metal particles in unusual locations on a carrier. In this regard, the physical form and interwoven arrangement of graphite nanofibers (GNF) generates a structure where all the metal particles are dispersed on the support surface. The networked structure of these materials allows for easy access of both liquid and gaseous reactants. As a consequence, more efficient interaction between the metal particles and reactant is achieved and problems associated with mass transport limitations are minimized.

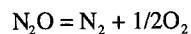
Key words: Catalyst supports, Graphite nanofibers, Supported copper catalysts

1. INTRODUCTION

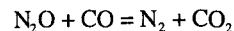
The structural architecture displayed by graphite nanofibers makes such materials extremely versatile as catalyst support media. The exposed surfaces of some of these materials consist entirely of graphite edges that are separated by a distance of 0.335 nm and these features provide a unique type of surface structure for the deposition of metal crystallites. Under these conditions the surface atoms of the metal crystallites adopt arrangements that are not generally encountered on other conventional support media, such as active carbon, silica or γ -alumina [1]. The carbon atoms in the graphite edge regions can adopt one of two arrangements, the so-called "arm-chair" and "zig-zag" conformations. Since the topography of the exposed carbon atoms in these two faces is different, one might expect the metal particles to adopt specific morphologies that are determined by the structure of the face onto which they nucleated. Indeed, it has been reported that when nickel particles were dispersed onto two types of graphite nanofibers, where it was suspected that different faces were exposed, diverse catalytic behavior was observed. In this case, the unexpected variations in reactivity and selectivity of the metal were attributed to differences in the crystallographic orientation of the catalyst particles resulting from interactions with the respective faces [2]. Some review articles have highlighted the modifications in both particle morphology and catalytic performance brought about by supporting metal crystallites on graphite nanofibers [3,4]. The first attempt to exploit the potential of these materials as catalyst support media was reported in 1994 [5]. In the current investigation we have used the decomposition of N_2O as a probe to compare the catalytic performance of copper supported on graphite nanofibers with that where the metal was dispersed on other forms of carbon. Although it does not belong to the same

category of pollutants as NO_x , N_2O has been identified as a contributor to the destruction of the ozone layer in the stratosphere and is recognized as a greenhouse gas. The emission of N_2O comes from both natural sources and is generated during the production of adipic acid and nylon.

The thermal decomposition of N_2O commences at 625°C and a number of metal oxides have been found to catalyze the reaction, however, the activity is not maintained for very long periods of time. The reaction is believed to proceed via an electron transfer mechanism, where the adsorbed oxygen species reacts with a similar entity to produce O_2 .



On the other hand, if a reducing agent such as CO is present, the oxygen species can react with the molecule to form CO_2 .



This latter reaction will enable one to circumvent problems associated with gasification of the graphitic support media that are encountered in the presence of pure N_2O at elevated temperatures.

2. EXPERIMENTAL

The graphite nanofibers used in this work were synthesized according to previously described procedures. A copper-nickel based catalyst was used to generate "herring-bone" like structures {GNF-H} from the decomposition of ethylene at 600°C [6]. "Platelet" graphite nanofibers (GNF-P) were grown from the decomposition of a CO/H_2 (4:1) mixture over an iron-based catalyst at 600°C [7]. The arrangements of the graphite sheets constituting the structures of these two types of graphite nanofibers are shown in the schematic diagram, Figure 1. Prior to use the respective catalyst

particles responsible for producing the nanofibers was removed by dissolution in dilute hydrochloric acid. The BET surface areas of the three support media were obtained from N_2 adsorption at -196°C with a Coulter Omnisorp 100CX unit and these data are presented in Table I. Also included in this table are the values for the corresponding supported 5 wt.% Cu catalysts.

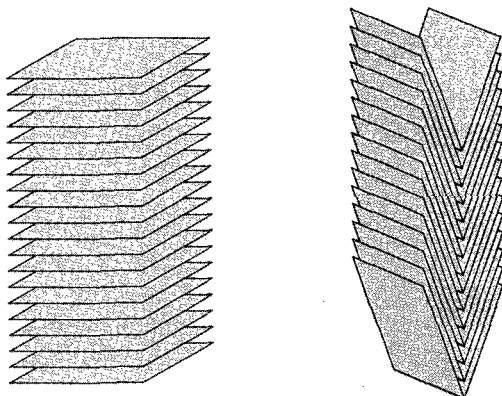


Figure 1. Schematic representation of the arrangement of graphite planes in the Platelet (left) and Herringbone (right) structures

Table I. BET N_2 surface areas of the pristine supports and corresponding 5 wt.% Cu catalysts

Support	Surface Area (m^2/g)	Surface Area of Catalyst (m^2/g)
PF	6	9
GNF-P	79	94
GNF-H	215	225

Finally, TEM and XRD techniques were used to examine these purified materials to ensure the complete removal of the original catalyst particles. The GNF supported copper catalysts were prepared according to a standard incipient wetness approach. Copper nitrate, dissolved in ethanol, was used as the precursor salt and was added to the support media in a drop-wise fashion. Following thorough mixing, the solvent was evaporated, the impregnated samples dried and calcined in air at 180°C for 20 hours. Finally, the catalyst powders were reduced in $10\%H_2/He$ at 300°C for 24 hours to achieve a 5 wt.% metal loading. A similar procedure was adopted to prepare a 5 wt.% copper dispersed on pitch-based carbon fibers (PF), which was used for comparative purposes.

The N_2O decomposition and reduction with CO reactions were performed in a custom designed fixed-bed micro-reactor system using approximately 100 mg catalyst to determine the activity. The feed gas mixture was regulated at a total flow of 50 ml/min using MKS mass flow controllers. In these experiments $10\%N_2O/He$ and $4\%N_2O/4\%CO/He$ respectively, were used as feedstocks. The gas phase products along with unconverted reactants were analyzed by an on-line gas chromatography unit equipped with a 5A molecular sieve column and a thermal conductivity detector.

3. RESULTS AND DISCUSSION

3.1 N_2O decomposition over Cu/Carbon catalysts

In the absence of a catalyst no decomposition of N_2O was detected at temperatures up to 600°C . The conversion of N_2O was calculated from the amount of N_2 versus the total feed of N_2O . As can be seen in Figure 2, while all the catalysts increased the activity for N_2O decomposition, the Cu/GNF-H system gave the highest activity and the lowest performance was observed with the Cu/PF catalyst. Comparisons of the product distributions over the various catalysts are listed in Table II, from which it can be seen that N_2 and CO_2 were the only products from this reaction. The formation of the latter product arises from the interaction of the surface oxygen species with the carbonaceous support materials. It is evident that this process becomes more severe as the temperature is progressively increased. There was also a tendency for the copper species to undergo oxidation and the combination of these two effects had a serious impact on the activity and stability of the catalyst systems.

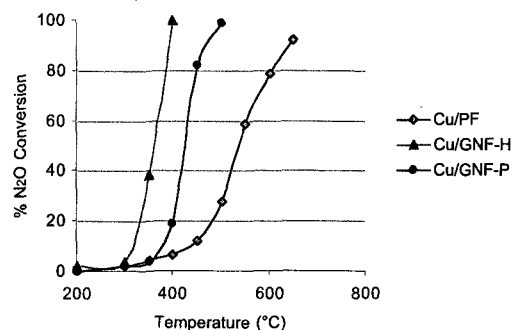


Figure 2. Effect of Carbon support on the copper catalyzed decomposition of N_2O .

Table II. Product distribution from decomposition of N_2O over 5% Cu/C catalysts

T $^\circ\text{C}$	% Products					
	GNF-H		GNF-P		PF	
	N_2	CO_2	N_2	CO_2	N_2	CO_2
200	100	-				
250	100	-	100	-		
300	70.8	29.2	100	-	100	-
350	66.7	33.3	82.3	17.7	74.8	25.2
400	66.8	33.2	72.0	28.0	68.4	31.6
450			68.3	31.7	69.8	30.2
500			66.4	33.6	70.0	30.0
550					68.4	31.6
600					68.8	31.2
650					66.6	33.4

3.2 N_2O - CO reaction over Cu/Carbon catalysts

The overwhelming advantage of performing the N_2O decomposition reaction in the presence of a reducing agent, such as CO, is that Cu is maintained in the active metallic state and the gasification of the carbon support is no longer a serious problem. A comparison of the catalytic activity of the three carbon supported Cu systems as determined from N_2O conversion as a function of temperature is presented in

Figure 3. A very low conversion of N_2O was found over Cu/PF and reached about 10% at 300°C. The activity remained quite stable at such a low conversion with the CO conversion being marginally lower than that of N_2O .

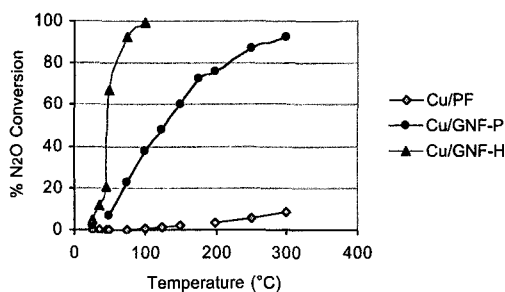


Figure 3. Effect of the carbon support on the copper catalyzed decomposition of N_2O in the presence of CO as a reducing agent.

In contrast, when Cu was dispersed on the graphite nanofibers extremely high catalytic activities were observed. Indeed, when the reaction was carried out over the Cu/GNF-H system, 100% conversion of N_2O was achieved at temperatures of around 100°C. Both nanofiber supported metal catalysts maintained their activity for prolonged periods of time, as can be seen from the plots shown in Figure 4. These data were obtained from the decomposition of N_2O/CO (1:1) over the respective nanofiber supported Cu catalysts at 50°C. The trend of catalytic activity can be correlated with the degree of metal dispersion [8], which was found to follow the sequence: Cu/GNF-H > Cu/GNF-P > Cu/PF.

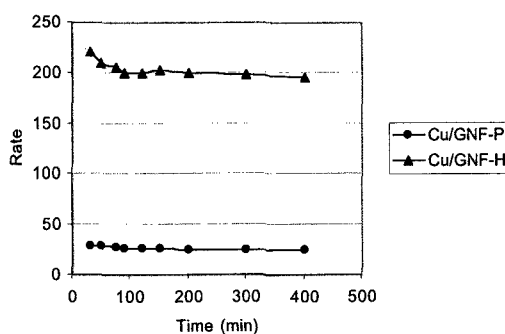


Figure 4. Activity as a function of time for the decomposition of N_2O/CO (1:1) over Nanofiber supported Cu.

Additional reaction studies were carried out over a Cu/GNF-H catalyst in order to investigate the behavior of the system under CO lean and rich conditions. CO was found to be capable of enhancing the rate of N_2O decomposition so that 100% conversion could be achieved at 50°C when the CO/N_2O ratio was close to 4. On the other hand, when the reactant mixture contained 10% excess N_2O the conversion only reached 83% at 100°C.

The observed high activity of Cu dispersed on the edge sites of graphite nanofibers is related to the metal particle morphology. Under these conditions the

particles adopt a thin, flat, faceted shape, which are characteristics general associated with the attainment of a strong-metal support interaction [9]. An example of the appearance of Cu crystallites located on the edge sites of graphite nanofibers is presented in the high-resolution TEM electron micrograph. This type of behavior is quite different to that encountered when the same metal is dispersed on pitch-based carbon fibers, which expose basal planes of graphite. In this case, the metal particles tend to acquire a globular geometry that is typical of systems where relatively weak interfacial forces exist between the metal and support [10]. Structural modeling of the arrangement of Cu atoms on the edge sites of graphite indicates the existence of a preferred crystallite orientation. It was found that $Cu_{(110)}$ exhibited the closest match with the graphite "zig-zag" face, whereas that of $Cu_{(100)}$ was in register with a section of the "armchair" face. It is conceivable that these two faces exhibit different reactivity patterns with respect to N_2O decomposition. One might argue that the GNF-H contains a higher fraction of $Cu_{(110)}$ faces, which is the most active state of the metal for the N_2O decomposition reaction.

3.3 N_2O decomposition over Carbon catalysts

In this set of experiments the catalytic performance of various carbon materials was evaluated for the N_2O decomposition. The conversion of N_2O was calculated from the amount of N_2 formed during the reaction under given conditions. A comparison of the performance of the various carbon materials as a function of temperature is shown in Figure 5. From these data it can be seen that the nanofibers exhibit the highest activity with the lowest conversions taking place over pitch-based carbon fibers. For comparison purposes the data obtained from passing N_2O through an empty reactor under otherwise identical conditions is included in this plot. The presence and nature of reactive edge sites is once again of paramount importance in determining the catalytic performance of the solid carbon catalyst.

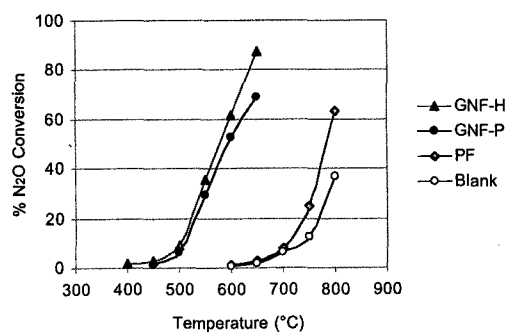


Figure 5. Comparison of the catalytic activity of metal-free carbon materials towards the decomposition of N_2O as a function of temperature.

3.4 N_2O - CO reaction over Carbon catalysts

A similar set of experiments to those described above was carried out in the presence of an equimolar mixture of N_2O and CO. Inspection of the results shown in Figure 6 indicates that the most active catalyst was GNF-H closely followed by GNF-P. On

the other hand, the performance of pitch-based carbon fibers in which the surface consists of a fraction of basal plane regions was very poor.

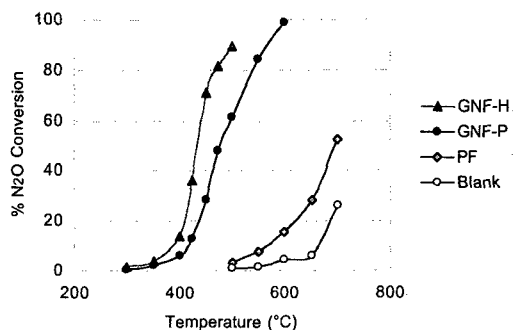


Figure 6. Comparison of the catalytic activity of metal-free carbon materials towards the decomposition of N_2O/CO (1:1) mixtures as a function of temperature.

4. SUMMARY

When Cu is supported on graphite nanofibers that expose a significant fraction of edge sites, the systems exhibit very high activity for the conversion of N_2O into N_2 . This degree of activity is not evident when the metal is dispersed on pitch-based carbon fibers where the surface consists almost entirely of graphite basal planes. All the carbon substrates, however, suffered from problems associated with gasification at high temperatures. The addition of an equimolar concentration of CO to the NO was found to promote the conversion reaction and at the same time inhibit the gasification of the carbonaceous support media. Finally, it was intriguing to discover that in the absence of dispersed Cu, the pristine graphite nanofiber materials functioned as effective catalysts for both these reactions. It is believed that the presence of functionalized edge sites in these unusual materials is responsible for the observed catalytic activity.

5. REFERENCES

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