

# Selective Catalytic Reduction of NO by Methane on Copper Catalysts: the Effects of Modifying the Catalysts with Acids on $\gamma$ -alumina

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This work compares the performance of copper catalysts modified with that of acids. Hence,  $\gamma$ -alumina is used to support the catalyst in the selective catalytic reduction of nitric oxide by hydrocarbons (HC-SCR) using methane at temperatures from 623-1023 K in the presence of oxygen. The copper catalysts were prepared by the incipient wet impregnation of a modified support of  $\gamma$ -alumina with copper nitrate, and by modifying the using nitric, acetic and phosphoric acids, respectively. The effectiveness of the transformation with nitric oxide over the catalysts, determined by comparing the conversion of nitric oxide with non-modified Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, to that by modified Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, implied that the reduction of transformation nitric oxide was most efficient when the catalyst modified with nitric acid. Modifying a copper catalyst with nitric acid markedly was found to increase the efficiency of reduction, whereas treatment with acetic and phosphoric acids did not promote the reduction of NO. However, a higher concentration of nitric acid corresponds to a higher efficiency of transformation nitric oxide; thus, converting nitric oxide using the catalyst modified with nitric acid is favored. Pre-treating the support  $\gamma$ -alumina with a higher concentration of acid solution promotes higher activity and greater acidity of the transforming nitric oxide reaction over a copper catalyst, because such pretreatment with acid enlarges the pores in the support, increasing the internal mass transfer and the reactivity over the catalyst. Notably, the presence of Cu (I) and Cu (II) at active sites may also affect the efficiency of the transformative reaction with nitric oxide. When the inlet gas is methane, the corresponding efficiency of the transformation nitric oxide shows that methane is an effective reducing agent.

**Keywords:** nitric oxide, acid modified, HC-SCR, methane, reducing agent

## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) are a very interesting and important family of air-polluting chemical compounds, and are increasingly attracting the interest of regulators in Taiwan. The primary

sources of nitrogen oxides, including several stationary industrial fossil fuel combustion processes or mobile sources, are of concern because these pollutants are significant precursors of both acid rain and acidification of the aquatic system, and because the pollutants react in the atmosphere to form ozone and photochemical smog (Huang et al., 1999). The many available technologies for reducing nitric oxide emissions can be classified as dry or wet processes. Complete biological treatment systems have been extensively investigated and

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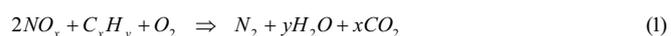
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implemented. Of these, the catalytic method is the most effective means of meeting present and future requirements, and is used in dry systems, including selective catalytic reduction (SCR), which involves ammonia, and selective non-catalytic reduction (SNCR), which involves ammonia or urea. Furthermore, modifications to combustion processes have been extensively examined and effectively implemented (Centi and Perathoner, 1995). SCR uses a catalyst and ammonia in the presence of oxygen to reduce nitric oxides to elemental nitrogen and water. It also has great potential for controlling emissions of nitric oxide, and is thus commonly performed in factories. However, its disadvantages include high operating temperatures (300~600 °C), the need for chemical additives, safety hazards and the emission of nitrous oxide (N<sub>2</sub>O), which is a harmful greenhouse gas (Zhu et al., 2000). In spite of these problems, the many benefits of SCR make it an attractive alternative control technique. Catalysts have a finite life in a flue gas, and some ammonia can pass through without reacting. The use of wet-scrubbing agents to adsorb nitric oxide enables alkali in water, water alone, or hydrogen peroxide to be used as the liquid for capturing nitric oxides (Burdeinaya et al., 1996). The biological treatment of nitric oxide is an inexpensive alternative technique, but it is only suitable for use in chemical processes (Liu et al., 1991; Chou and Lin, 1998; Ye et al., 1994). The main drawbacks of such biological treatment processes include the high gas empty-bed retention time, the expense of the required nutrient additives and the degradation of the biofilm.

The catalytic reduction of nitrogen monoxide (NO) in an air stream represents an alternative technique to the fuel combustion and chemical process; it allows the flue gas to flow with minimum resistance and a minimum drop in pressure, maximizing the surface area of the catalyst. Using a catalyst to cause combustion to occur below the NO formation temperature can

appropriately limit temperature. Metal oxide catalysts, including iron oxide-based catalysts and vanadium oxide supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or SiO<sub>2</sub> have been demonstrated to exhibit a high activity in terms of the SCR of NO in the presence of a large excess of oxygen (Wong and Nobe, 1986; Tufano and Turco, 1993). During recent years, much research on the use of copper-based catalysts in the conversion of nitrogen oxides has been presented. Most has focused on developing selective NO reduction with hydrocarbons, such as methane, propane and propene. Zeolite- and alumina-supported catalysts have also been extensively studied (Desai et al., 1999; Moretti et al., 1999). The reduction of NO by methane in the presence of oxygen generally proceeds as follows.



Centi and Perathoner (1995) published an excellent review of the chemistry of copper-based catalysts, in which they indicated avenues for future research. Copper-containing catalysts (zeolite- and oxide-based catalysts) can be used as the active catalytic decomposition phase in catalytic processes because they are shape-selective in a broad variety of reactions. Accordingly, catalytic reduction is a new process for reducing nitrogen oxides, and the catalysts employed are effective at higher temperatures than conventional catalysts. Consequently, many researchers have begun to focus on NO decomposition (Tomasic et al., 1998; Pietrogiacomini et al., 1999; Chen et al., 1999). However, these studies involve too much uncertainty about the chemical mechanisms of the catalytic reduction of NO. Additionally, the catalytic reduction of NO deserves further investigation because in air streams, it has yielded only limited results. Appropriate treatments of

catalysts with acids modify the acidity and texture of the catalysts to increase both their specific surface area and the number of useful acid active centers (Shouro et al., Wang et al., 1998). Therefore, the treatment of catalysts with acid has been extensively investigated over recent years to accelerate the decomposition of NO under moderate reaction conditions.

However, the decomposition of NO on the acid-modified Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has not been deeply considered. Given the world's extensive supply of natural gas (NG), methane would certainly be a preferred hydrocarbon for use in the non-selective reduction of NO. Hydrocarbons also represent attractive alternative reducing agents to ammonia (Armor, 1995). Thus, this study focuses on the involvement of metal oxide catalysts, which exhibit significant catalytic activity in the selective reduction of NO by hydrocarbons, (HC-SCR), in this case methane on Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The effects of three types and three different concentrations of inorganic acid, including nitric acid, phosphoric acid and acetic acid solution used to treat a  $\gamma$ -alumina support, on the reduction of NO, were also investigated. This study presents the results of laboratory studies of the catalytic reduction of NO over copper catalysts in a stream of air, and reports the activity of Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with various loadings of copper, as prepared by the incipient wetness impregnation method. Accordingly, the activities of the prepared catalysts were evaluated and the superior catalyst was chosen. The catalysts were also characterized by BET, TGA, triethylamine-TPD, XRD and SEM, to provide further insight into the increase in activity associated with treatment with acid.

## 2. Materials and Methods

An  $\gamma$ -alumina support (Showa Chemicals INC., Tokyo, Japan, 99%) was initially treated with acidic solutions of various concentrations. The

acidic solutions included three different types and various concentrations of inorganic acid, ranging from 0.5 M to 6 M. They were nitric acid, phosphoric acid and acetic acid. In each batch, 10g of  $\gamma$ -alumina were poured into a flask that contained 50 ml of an acidic solution. The mixture was then heated to 373 K and mechanically stirred for 2 hr, before being cooled to room temperature. The acid-treated alumina samples were then washed in distilled water and dried overnight in air at 378 K for 24 hr. They were then calcined in an oven with an air supply at 823 K for 10 hr. The acid-treated alumina thus prepared was used as a support, and the pH values of the aqueous slurries of alumina were also measured. The acid-treated supports were Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-nitric-acid-treated, Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-phosphoric-acid-treated or Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-acetic-acid-treated. In cases of extended treatment, the acid solution was replaced with a fresh solution every hour.

In this study, incipient wetness impregnation was used to produce acid-treated alumina with various copper contents from 2 to 10 wt% Cu. A volume of highly pure copper nitrate (Merck, Darmstadt, Germany, 99.5%) was dissolved in an amount of water equal to the pore volume of the supports. The solution was dispersed uniformly on the well-impregnated supports, which were dried at 378 K for 24 hr. The catalysts were then calcined in the oven for 10hr with an air supply at 823 K. For comparison, untreated catalysts were also prepared using bare alumina as the support.

Specific surface areas and total pore volumes specified by determined adsorption isotherms characterized the texture and structure of these catalysts. The distribution of pore sizes was determined as follows. First, the specific surface areas of the catalysts were measured by nitrogen adsorption-desorption, using a BET surface area analyzer (ASAP 2000, Micromeritics, Norcross, Georgia). Table 1 presents the compositions and properties of the prepared catalysts. X-ray

**Table 1.** Surface area and texture of untreated catalysts, determined by BET.

Catalyst Type	Treatment Conditions	BET S.A. (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (Å)
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	No treatment (original)	194	0.20	19.3
2 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	No treatment (original)	183	0.21	22.1
5 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	No treatment (original)	179	0.20	22.1
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	No treatment (original)	178	0.18	21.9
10 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	No treatment (original)	177	0.19	21.8

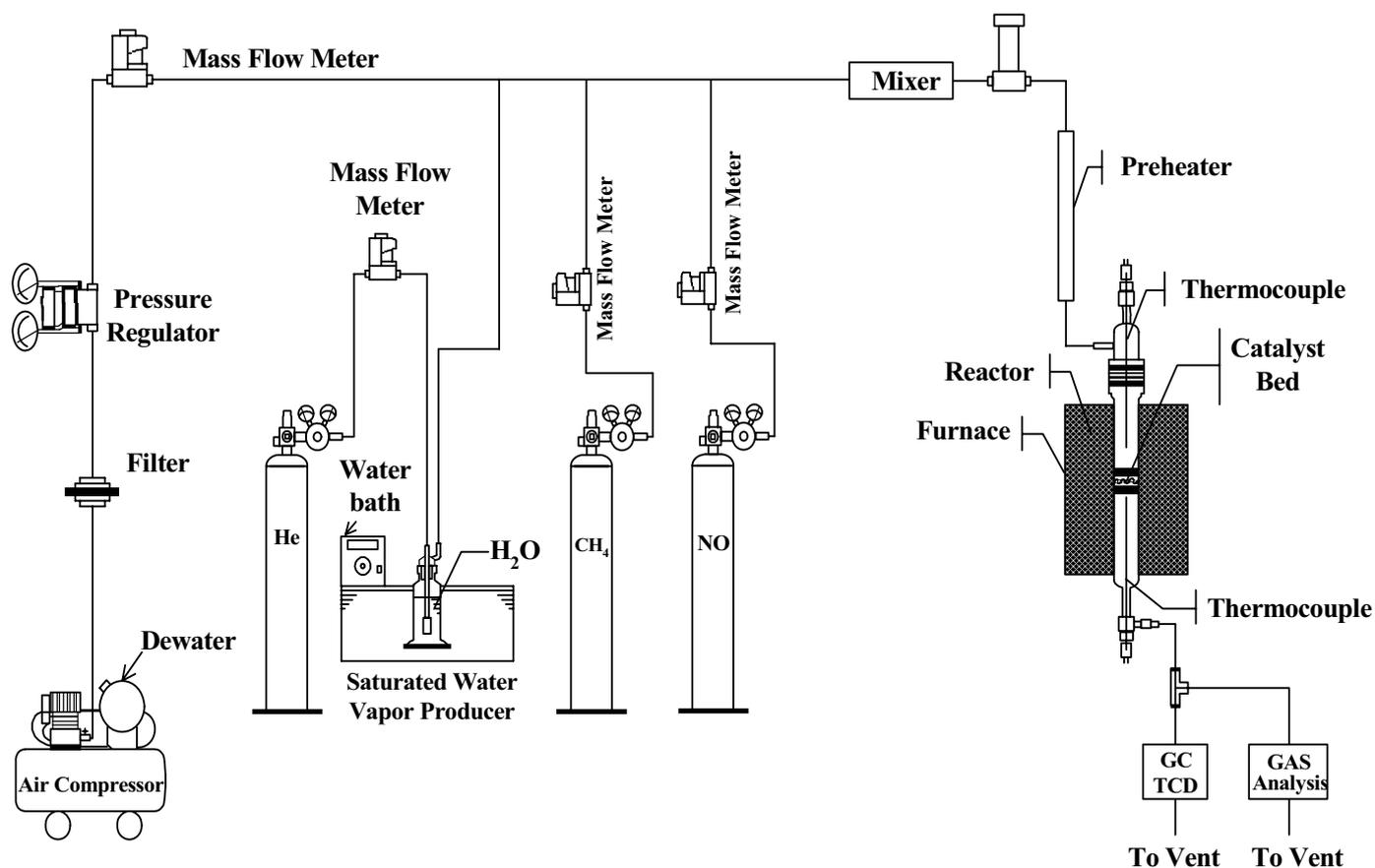
diffraction patterns were obtained using a Diano-8536 diffractometer with CuK $\alpha$  radiation as the source. During analysis, the sample was scanned from 20 to 80° at a rate of 0.4°/min. Scanning electron microscopy with an energy dispersive X-ray spectrometer (SEM/EDX, JEOL, JSM-6400, KeveX, DeltaII), elucidated the morphology of the catalysts and provided information on the distribution of copper on the catalyst surface. Hence, copper-based catalysts prepared by incipient wetness impregnation were found to exhibit various activities in the conversion of NO. The different copper species in these catalysts are responsible for this divergence. Thermogravimetric analysis (TGA) experiments were conducted in a TGA unit (TGA-50, Shimadzu, Kyoto, Japan) at a heating rate of 283 K/min.

The effect of acidity and the characteristics associated with the modification of the catalysts using acid were measured in temperature-programmed desorption (TPD) experiments on triethylamine. These experiments were conducted in a vertical tube furnace with He as the carrier gas, according to a method similar to that of Shouro et al. (2000). Triethylamine is favorable as the probe used in the TPD analysis of mesoporous materials since it can easily migrate into the mesopores. A 0.1 g sample was placed in a quartz tube and dehydrated in a stream of helium at 1023 K for 3 hr. Triethylamine was adsorbed at 373 K for 2 hr and physisorbed triethylamine was extracted (at 373 K for 2 hr). The system was heated to 773 K at a rate of 60 K/min in the stream of helium, and the

amount of desorbed triethylamine was analyzed using a chromatograph (GC-14A, Shimadzu, Kyoto, Japan) equipped with a thermal conductivity detector.

Experiments were performed on a tubular fixed-bed flow quartz reactor (TFBR). Three flowing gases, NO, CH<sub>4</sub> and O<sub>2</sub>, were used in the preparation of the feeding mixture and the diluent's gas, helium, at the inlet of the reactor. Each gas was independently controlled using a mass flow regulator. Highly pure, dry air was used as the carrier gas, and its flow rate was controlled using a mass flow meter (830 Series Side-Trak<sup>TM</sup>, Sierra, Monterey, CA, USA) at 8-13 L/min. The mass of the catalysts was 1g (at an empty bed volume of approximately 1.2 cm<sup>3</sup>). External mass transfer and inter-particle diffusion were effectively unlimited in this reactor. The reaction tube (300 mm long with an inner diameter of 28mm) was placed inside a split tube furnace, along with the tube that contained the catalyst. Two thermocouples of type K (KT-110, Kirter, Kaohsiung, Taiwan), each with a diameter of 0.5 mm, were mounted and equally spaced along the catalyst bed. The thermocouples were also connected to a PID controller (FP21, Shimaen, Tokyo, Japan) that kept the temperature in the tube within  $\pm 0.5$  %. The feed gas (GHSV, 108000 ml/h-g) was maintained at concentrations of 1000 ppm NO and 1000 ppm CH<sub>4</sub>, and 2% O<sub>2</sub>. The catalyst was not deactivated during testing. Figure 1 schematically depicts the tubular fixed-bed reaction system (TFBR).

Samples before and after the reaction were

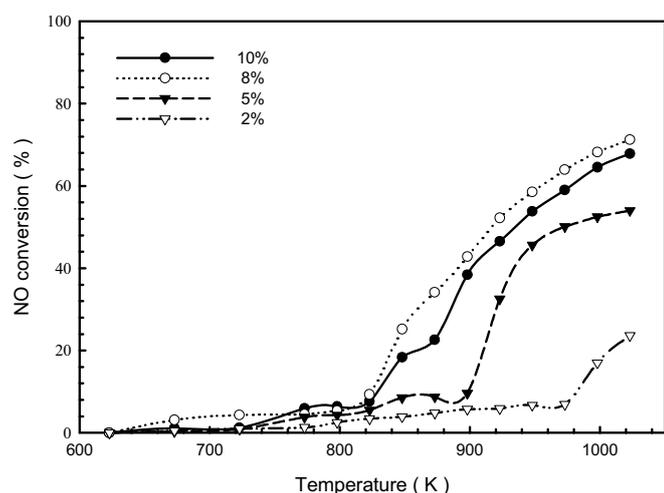


**Figure 1.** Schematic diagram of the tubular fixed-bed reaction (TFBR) system.

automatically injected through a sampling valve into a gas chromatograph (GC-14A, Shimadzu, Kyoto, Japan) equipped with a thermal conductivity detector. A stainless-steel column (Porapak Q 80/100mesh) was used to separate and analyze the concentrations of  $N_2O$  isothermally at 373 K. The gas  $CH_4$  was automatically injected before and after the reaction using a sampling valve into a gas chromatograph (Shimadzu GC-14A) equipped with a thermal conductivity detector. The areas under the signal peaks were measured electronically using a data integrator (CR-6A, Shimadzu, Kyoto, Japan). The concentrations of NO,  $NO_2$  and  $O_2$  in the gas samples were measured using a portable flue gas analyzer (IMR-3000, Neckarsulm, Germany), which was (linked to the designed location to enable continuous monitoring during combustion. Gas samples with known concentrations of NO were used to calibrate the analyzer.

### 3. Results and Discussion

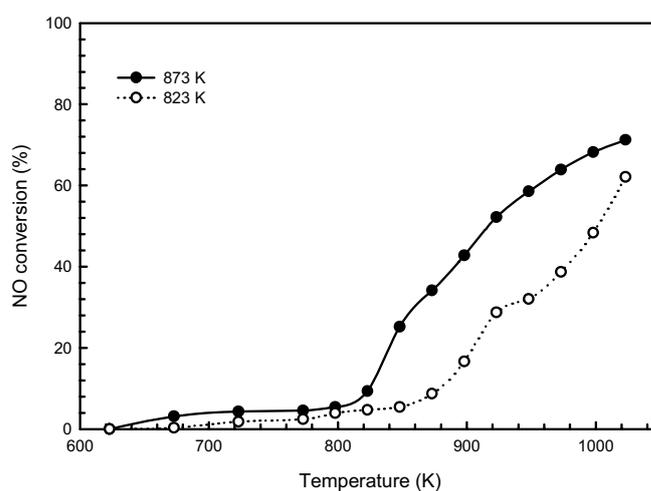
The capacity and texture of a catalyst's exterior surface strongly affects its adsorptive and catalytic behavior. Table 1 summarizes the characteristics of the test catalysts, as determined by BET (Brunauer-Emmett-Teller method) analysis, including specific surface area, pore volume and the mean diameter of their pores. The specific surface area, pore volume and mean diameter of the pores were  $194 \text{ m}^2/\text{g}$ ,  $0.2 \text{ cm}^3/\text{g}$  and  $19.3 \text{ \AA}$ , respectively, for the  $\gamma$ -alumina support. Increasing to 823 K the calcining temperature of a series of supported 2~10 wt.% Cu/ $\gamma$ - $Al_2O_3$  catalysts that had not been pretreated, reduced their surface areas ( $177\sim 183 \text{ m}^2/\text{g}$ ), slightly reduced their pore volumes ( $0.18\sim 0.21 \text{ cm}^3/\text{g}$ ) and very slightly increased their average pore diameters ( $21.8\sim 22.1 \text{ \AA}$ ). This test indicated that increasing the temperature at which the catalysts were calcined enlarged the lattice surfaces )of copper, whose



**Figure 2.** Effect of copper loading on the Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : 1000 ppm NO in He, 1000 ppm CH<sub>4</sub> in He, O<sub>2</sub> = 2%, GHSV = 108000 ml/h-g.

consequently higher loadings resulted in metal sintering, and a consequent reduction in catalytic activity.

Figure 2 shows the effect of copper loading on the conversion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at various temperatures. The figure shows that the maximum activity increases with copper loading in the range of 2 to 10%, and the reaction conditions strongly affect the relationship between the activity of the catalyst and copper content. However, the conversion of NO is a maximum over a loading of 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and is lower at excess copper loading (10%), because the side reaction of hydrocarbon combustion along with higher loadings cause metal sintering. Besides, the literature states that bulk CuAl<sub>2</sub>O<sub>4</sub> species can be formed by increasing the copper content to 10 wt.% (Chen et al, 1999). However, the copper species may change as a function of copper loading. Centi (1995) showed that increasing the copper content loading of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> causes charge to be transferred from isolated copper ions to a defect surface of copper aluminate and then to paracrystalline and crystalline CuO. Thus, in this study 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was selected as optimal in the



**Figure 3.** Effect of calcinations temperature on the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : 1000 ppm NO in He, 1000 ppm CH<sub>4</sub> in He, O<sub>2</sub> = 2%, GHSV = 108000 ml/h-g.

following.

With reference to the properties of catalysts modified using the three acids at the various concentrations listed in Table 2, as the concentration of nitric acid increased from 0.5 M to 6 M over 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the surface areas decreased, and the pore volumes and average pore diameters both increased substantially. Clearly, acidification participates importantly in activating the surface produced by treatment with acid, but the increase in the surface area may not dominate the increase in activity, and this question warrants further study. Hence, although increasing the concentrations of an acid may increase the diameter and volume of the pores, it can not increase the surface area, probably because excess copper on the surface of the catalyst inhibits such a change. Table 2 states that the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst modified with nitric acid had the highest surface area (174 m<sup>2</sup>/g); the one modified with acetic acid (168 m<sup>2</sup>/g) had the next highest surface area, and the one modified with phosphoric acid (162 m<sup>2</sup>/g) had the least surface area. Modification with nitric acid was also more effective than with

**Table 2.** Area and texture of catalysts after treatment with acid, determined by BET.

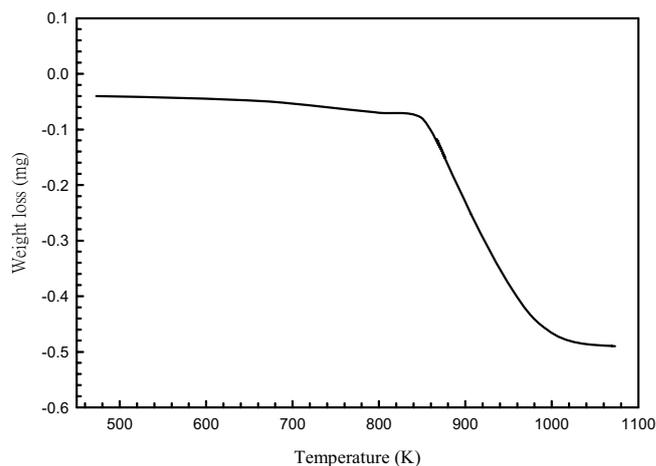
Catalyst Type	Treatment Conditions	BET S.A. (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (Å)
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.5 N-nitric-acid-treated	191	0.21	22.3
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2 N-nitric-acid-treated	174	0.24	27.8
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	6 N-nitric-acid-treated	127	0.35	55.2
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2 N-phosphoric-acid-treated	162	0.19	20.8
8 wt.% Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2 N-acetic-acid-treated	168	0.16	19.3

the other two inorganic acids in increasing the pore volume and the average diameter of the pores in the Cu-oxide catalyst. Accordingly, pretreatment of the catalyst also influences the characteristics of its surface.

Figure 3 presents the effect of NO conversion at various calcination temperatures. The figure shows that the rate of conversion of NO increases with the calcination temperature in the range 823-873 K. The results were observed in the CH<sub>4</sub>-SCR reaction using the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, wherein the NO conversion rate exceeded 71.2% at 873 K. Consequently, higher calcination temperatures correspond to a higher conversion yield. Additionally, the textures of the catalysts were observed also to depend on the copper loading and

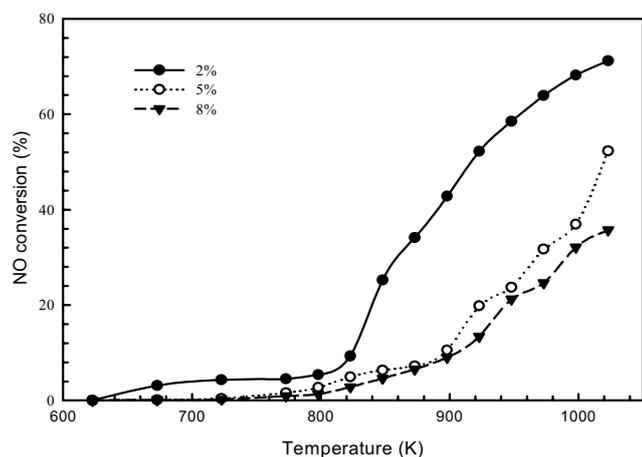
the calcination temperature. However, the effect of texture on activity requires further investigation. Recently, Centi et al. (1995) observed isolated copper ions and highly dispersed Cu<sup>2+</sup> clusters in samples calcined between 400 and 600°C. Figure 4 summarizes the results of TGA thermal decomposition of the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst does not lose mass until a temperature of approximately 873 K is reached. Above this temperature, a significant loss of mass may contribute to the decomposition and desorption of oxygen and water, implying that the amount of converted NO increases with the calcination temperature, below 873 K.

Oxygen is known to promote the chemisorption



**Figure 4.** Thermal gravimetric analysis (TGA) diagram of 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : Sample weight = 25 mg, heating rate = 283 K/min in nitrogen flow.

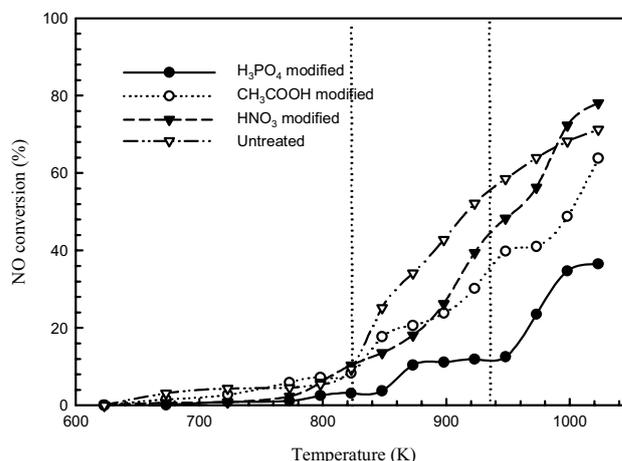
of NO and its reduction over oxides, increasing the rate of conversion of NO; the activity later declines but remains higher than in the absence of oxygen. Accordingly, copper oxides based on alumina have been found to be active in the selective reduction of NO with hydrocarbons/O<sub>2</sub> (HC-SCR). However, the effect of oxygen concentration must be considered. Figure 5 plots the effect of copper loading on the amount of conversion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at various temperatures. The figure shows that activity increases as oxygen concentration decreases from 8 to 2%, but that the conversion of NO is maximum at a concentration of approximately 2%. The oxidation of NO, considered to be a key step in the reaction that occurs when gaseous oxygen is fed into the system



**Figure 5.** Effect of oxygen concentrations on the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : 1000 ppm NO in He, 1000 ppm CH<sub>4</sub> in He, O<sub>2</sub> = 2%-8%, GHSV = 108000 ml/h-g.

with NO, is not directly involved in the reduction of NO. Centi (1995) showed that the oxidation of NO to NO<sub>2</sub> is the first step in the reduction of NO to N<sub>2</sub> and is performed during the conversion of NO by hydrocarbons in excess oxygen. Indeed, the presence of oxygen also affects the relative significance of all surface reactions, yet the valence state of the copper catalyst remains unchanged.

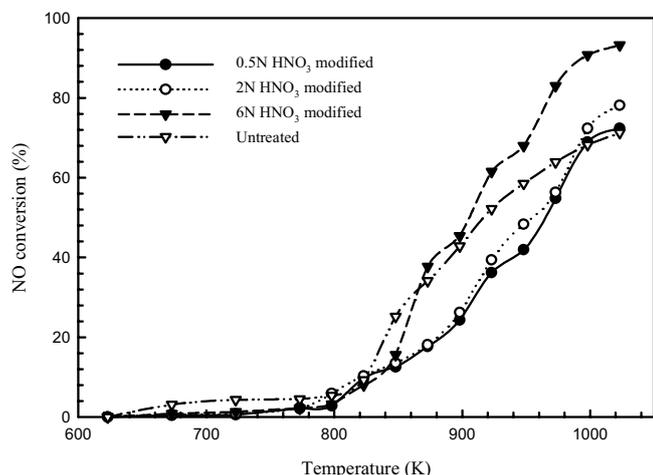
Catalytic activity varies with the composition and temperature of the catalyst. Figure 6 compares the efficiency of the reduction of NO by methane over 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified by the three acids at a fixed concentration of 2 M. Adding methane negligibly increases the rate of conversion of NO. In the first stage of the reaction, at temperatures between 823 K and 948 K, the Cu-oxide catalysts modified by nitric acid yield a conversion rate in De-NO of approximately 50% of that obtained with the original 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst or the other two types of catalyst. During the second reaction stage, at temperatures ranging between 948 K and 1023 K, the optimal conversion in De-NO with methane was approximately 80% of that obtained with the catalyst modified by HNO<sub>3</sub>. This result implies that the modification of the



**Figure 6.** Effect of treatment with different a fixed concentration (2M) of various inorganic acids on the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : 1000 ppm NO in He, 1000 ppm CH<sub>4</sub> in He, O<sub>2</sub> = 2%, GHSV = 108000 ml/h-g.

catalyst with acid is the crucial cause of the conversion of NO. Consequently, the decomposition of NO was slightly increased on the acidified Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 1023 K. This phenomenon was observed when the catalyst support was treated with HNO<sub>3</sub> because NO<sub>3</sub><sup>-</sup> had been decomposed during the preparation of the catalyst (which was calcined at 823 K). This enhancement in the rate of decomposition follows from the presence of additional acidic sites on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> when NO molecules are adsorbed. The inhibition of this effect, associated with treatment with phosphoric acid may be related to the formation of aluminum phosphate, which changes the composition and structure of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, as described in relevant literature (Wang et al., 1998).

The factor that critically affects the efficiency of removal of NO by SCR is the CH<sub>4</sub>/NO<sub>x</sub> ratio. The reaction equations indicate that the stoichiometric ratio of CH<sub>4</sub> to NO<sub>x</sub> is 1:1. Therefore, the amount of injected methane must be stoichiometric, to ensure maximum NO<sub>x</sub> reduction. Moreover, Armor (1995) also proposed the reduction of NO<sub>x</sub> by CH<sub>4</sub> in the presence of excess O<sub>2</sub> included the formation



**Figure 7.** Effect of treatment with various concentrations of nitric acid on the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of NO with CH<sub>4</sub>. Test conditions : 1000 ppm NO in He, 1000 ppm CH<sub>4</sub> in He, O<sub>2</sub>=2%, GHSV = 108000 ml/h-g.

of CH<sub>3</sub>· radicals as a key step, and a nitro species as an intermediate. Accordingly, the reducing agent and the active reaction temperature range of the catalyst are both factors that importantly impact the reduction of NO over copper-based catalysts modified with various acids. Notably, the impregnated 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is the most active in SCR during the conversion of NO in the presence of excess oxygen.

Figure 7 plots the effects of the 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst modified with nitric acid at various concentrations on the conversion of NO by methane at various temperatures under the same operational conditions as listed in Fig.6. The results show that the conversion of NO increased sharply with the concentration of nitric acid from 0.5 N to 6 N, when a modified catalyst was used at temperatures between 800 K and 1023K. Nitric acid is a strong oxidizing reagent with a strong electrochemical tendency, corresponding to the generation of acidic functional groups on the surface of alumina when treated with this acid (Teng et al., 2001). The reduction of NO causes the extent of conversion to increase with the number of acidic sites on the surface of the alumina, resulting

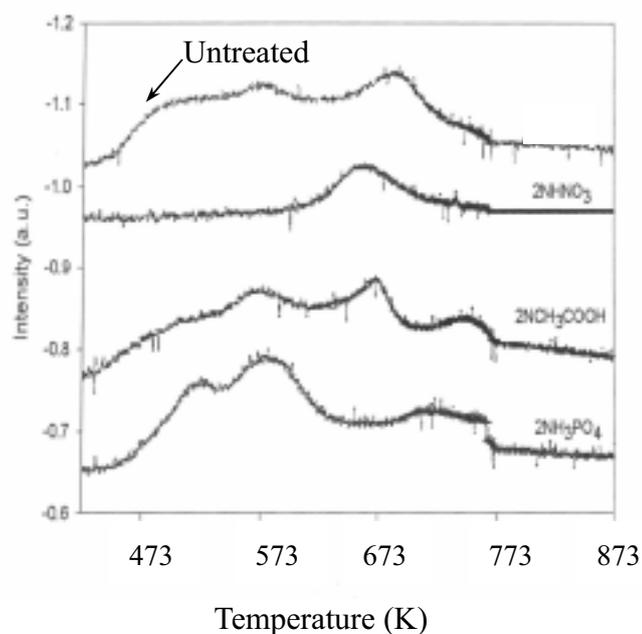
**Table 3.** Slurry pH of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports.

Catalyst Sample	PH <sub>slurry</sub>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	8.24
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ( 0.5 N-nitric-acid-treated )	3.25
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ( 2 N-nitric-acid-treated )	2.84
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ( 6 N-nitric-acid-treated )	2.43
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ( 2 N-phosphoric-acid-treated )	4.67
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ( 2 N-acetic-acid-treated )	4.81

in the adsorption of methane at the acidic sites in a heterogeneous reaction. Also, acidic sites are generally considered to be the active centers of a number of reactions known to be catalyzed by catalytic surfaces (Xie et al., 2000).

Table 3 presents the pH of the acid-modified aqueous slurry. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is seen to exhibit basic properties. The sample treated with 6 M nitric acid is the most acidic, which result is consistent the literature (Zhu et al., 2000). Consequently, the activity of the catalyst modified with 6 M nitric acid was considerably improved, as shown by conversion rates of over 90% from nitric oxide to nitrogen at 1023 K, with a spatial velocity of 108,000 h<sup>-1</sup>; the addition of methane clearly promotes the conversion of NO.

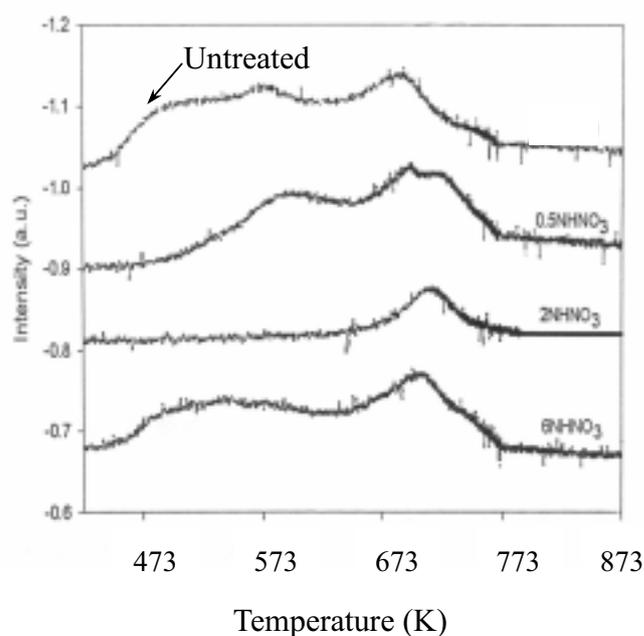
Figure 8 plots the variations of TPD desorption intensity associated with 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with various inorganic acids. The temperature at which the peak desorption occurs is related to the adsorption strength. Nitric acid caused intense surface oxidation, revealed by the evolution of an amount desorption from the surface of the tested catalysts, implying that the conversion rate of NO is high in reduction over Cu-oxide catalysts modified with 2 M nitric acid. At temperatures above 773 K, the amounts of triethylamine evolved with the four catalysts are similar. The difference between the extents of the



**Figure 8.** TPD of triethylamine profiles of 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts that are untreated or treated with various inorganic acids.

evolution is greatest below 773 K. A reduction of approximately 80% of the NO with methane was observed over the catalyst modified with 2 M nitric acid at 1023 K (Fig. 6). Therefore, pre-treating the support alumina with acid encourages the activity in the De-NO reaction over a copper catalyst, because pretreatment with acid enlarges the pores in the support, increasing internal mass transfer and the reactivity over the catalyst. The local charge separation and weakening of the N-O bond probably drives the decomposition of NO. However, treatment with acid may plug the micropores of the supports, because most pores that are blocked by catalyst particles are micropores. Notably, the enhancement by acid pretreatment of the production of various types of copper ions with active acidic oxygen functional sites (oxygen-copper complexes) may also promote the adsorption of methane. Hence, copper-based catalysts modified with nitric acid are active in transforming nitric oxide.

Figure 9 summarizes the variations of TPD desorption intensity of 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

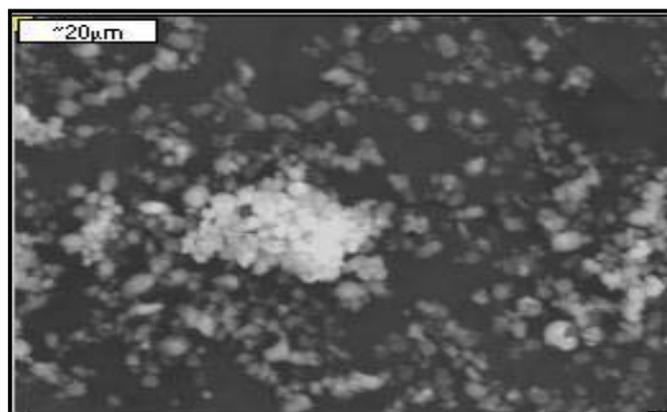
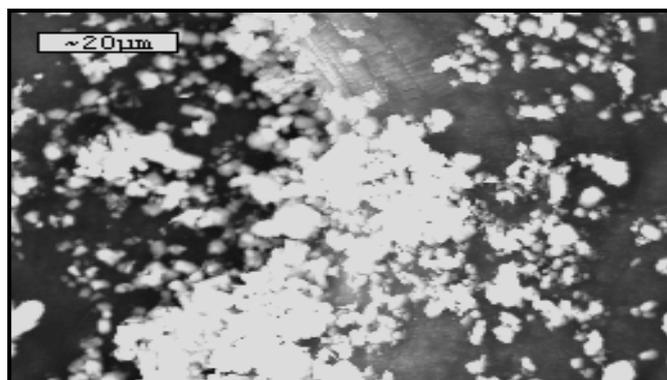


**Figure 9.** TPD of triethylamine profiles of 8 wt.% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts that are untreated or treated with various concentration of nitric acid.

modified with nitric acid, to present the results concerning catalysts modified with nitric acid at various concentrations, as listed in Fig. 7. Experimental results reveal that nitric acid at high concentration causes the evolution of triethylamine from the surface of the test catalysts and yield a broad peak in the range 673-773 K. This result implies that the rate of conversion of NO during reduction is greater over Cu-oxide catalysts with more acidic surface groups. A lower temperature is required to enable the desorption of triethylamine from more weakly acidic sites, whereas a higher temperature (713 K) is required for desorption from more strongly acidic site. Approximately 93.2% reduction of NO with methane was observed over a catalyst modified with 6M nitric acid at 1023 K. Clearly, acid treatments formed surface oxygen complexes that promote NO conversion; these complexes evolve into triethylamine at low temperatures (<773 K). Similar results have been reported elsewhere (Teng et al., 2001; Zhu et al., 2000). Thus, pre-treating the support alumina with a more concentrated acidic solution increases

activity in the De-NO reaction over the copper catalyst. Hence, copper-based catalysts modified with nitric acid are active in transforming nitric oxide. Notably, the active sites of the surface copper species the catalysts were determined by X-ray diffraction (XRD) to be Cu (I) and Cu (II), which might also determine the efficiency of the De-NO reaction. NO was adsorbed onto  $\text{Cu}^+$  cations and decomposed *in situ* into molecular nitrogen and  $\text{Cu}^{2+}$ -coordinated oxygen. Oxygen that bridges two copper sites is easy to abstract. Typically, hydrocarbons regenerated at the active site may react vigorously with surface oxygen. Recent results published by Moretti et al. (1999) indicate that the most active copper sites might be dimeric ( $\text{Cu}_2\text{O}_2^{2+}$ ) or those of  $\text{Cu}^+\dots\text{Cu}_2^+\dots\text{O}^-$  species, probably bonded to next-nearest-neighbor framework  $\text{AlO}_4^-$  species. As a result, the efficiency of De-NO mixing obtained when the inlet gas is mixed only with methane implies that methane is a good reducing agent. Accordingly, in this study, alumina-supported copper catalysts modified with acid are shown to be highly active in the catalytic decomposition of NO in a reductive environment.

The surface morphological changes of copper loaded  $\gamma\text{-Al}_2\text{O}_3$  were elucidated by scanning electron microscopy to provide further information concerning the status of the copper species in these catalysts. Figure 10 illustrates the surface structure of an acid-treated Cu/ $\gamma\text{-Al}_2\text{O}_3$  catalyst. Figure 10 (a) shows that the surface of the Cu/ $\gamma\text{-Al}_2\text{O}_3$  catalyst is more aggregated and crystalline than that depicted in Fig. 10 (b). Figure 10 (b) shows that the disaggregation and dispersion phases were formed by the direct removal of metal ions by the acidification of the surface of the catalyst, implying that the porosity of the particles changed. These crystal phases may explain the high activity of the catalysts. The results also confirm that the dispersion of the catalyst increases the efficiency of removal of NO by methane.



**Figure 10.** SEM photograph of the outward appearance of dispersed metal white point of 8 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$  catalyst that is (a) untreated and (b) that is treated with 6 M nitric acid.

#### 4. Conclusions

This study examines the effects of treating, with three inorganic acids at various concentrations, a series of copper-based catalysts, on the conversion associated with decomposition of NO with hydrocarbon (HC-SCR). Reactions with methane are investigated, methane is found to support the efficient conversion of NO. The 8 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$  catalyst modified with nitric acid is more active in modifying the catalyst than one modified by either of the other two acids. The rate of conversion of NO increased sharply with the concentration of nitric acid from 0.5 M to 6 M in a modified catalyst at temperatures from 800 K to 1023 K. The extent of promotion of NO decomposition may be associated with the number of additional acid centers on the acidified catalyst that can trap NO molecules. A higher concentration of nitric acid is

associated with greater desorption from the surface of the test catalysts, and thus more extensive conversion during the reduction of NO than that associated with a copper-based catalyst modified with nitric acid at a concentration of 6 M. This enhancement is related to the additional acid sites and greater acidity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that adsorbs NO molecules. A reduction of about 93.2% of the NO can be achieved over the catalyst modified with nitric acid at a concentration of 6M at a temperature of 1023 K.

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