



مجموعه مقالات

چهارمین همایش ملی کاربرد فناوری هسته‌ای در علوم کشاورزی و منابع طبیعی
(۲۹-۳۰ اردیبهشت، ۱۳۹۴، پژوهشکده کشاورزی هسته‌ای)

The 4th National Congress on Nuclear Technology Application in Agricultural & Natural Resource Sciences (19-20 May, 2015, Nuclear Agriculture Research School)

تهیه نانو کامپوزیت زیست سازگار جهت مطالعه تبدیل یون های نیترات از پسمان های هسته ای

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چکیده: نمونه های زیروژل زیست سازگار از هیدرولیز و تراکم تترا اتیل اورتو سیلیکات و با روش سل-ژل تهیه می شود. در این تحقیق؛ نسبت مولی جدید تترا اتیل اورتو سیلیکات/آب=۱۱٫۷ برآورد می شود. هم چنین مقادیر لازم نیترات مس ۳ آبه و سولفات مس ۵ آبه به محلول افزوده شده تا غلظت اکسید مس در محلول نهایی به ۱۲-۱۰ درصد وزنی برسد. پس از عملیات خشک سازی در محیط عادی؛ نمونه ها در دما های ۴۰۰ و ۶۰۰ و ۸۰۰ درجه سانتی گراد حرارت می یابند. خواص ساختاری توسط میکروسکوپ الکترونی عبوری؛ آنالیز سطح ویژه و روش های کاهش حرارتی در دماهای مختلف خصلت یابی می گردد. در نهایت خصلت نانو کامپوزیت ها با استفاده از کاهش کاتالیتیکی انتخابی آمونیاک و بدنبال آن تبدیل یون های نیترات به مونو اکسید نیتروژن در فاز گازی انجام می شود. نتایج مطالعه؛ کاهش سیستماتیک مونو اکسید نیتروژن توسط آمونیاک بر روی نانو کامپوزیت اکسید مس بر بستر سیلیکا در پسمان های هسته ای را تایید می نماید که این به منظور توانایی این ترکیبات به تبدیل گونه های غیر مضر زیست محیطی در دما های مختلف می باشد.

کلمات کلیدی: اکسید مس؛ فعالیت کاتالیتیکی؛ نانو کامپوزیت؛ کاهش مونو اکسید نیتروژن؛ فاز گازی

Preparation of Co-Environmental Nano-Composites for Conversion Studying of Nitrate Ions from Nuclear Effluents

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ABSTRACT: The co-environmental xerogel samples were prepared by hydrolysis and condensation of tetraethyl ortho-silicate (TEOS) by the sol-gel method. In this investigation, a new molar ratio of H₂O/TEOS was determined to be 11.7. Also, the necessary amounts of tri-hydrated copper nitrate and penta-hydrated copper sulfate were added to the solution in such a manner that the concentration of the copper oxide in final solution reach to 10-12 wt %. After ambient drying, the xerogel samples were heated at 400, 600, and 800°C at a slow heating rate (50°C/h). The structural properties were characterized by Transmission Electron Microscopy (TEM), Brunauer, Emmett and Teller theory for specific surface area determination (BET) and Thermal Program Reduction (TPR) methods at different temperatures. Finally, characterization of nano-composites was studied for NH₃ selective catalytic reduction (NH₃-SCR) of nitrate ions and following it to NO_x (X=1) in gas phase. The results were presented the systematic reactivity study of NO reduction by NH₃ on dispersed copper oxide nano-composites over silica supports, in order to



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determine the ability of these materials to conversion into environmental harmless species at different temperatures.

Keywords: Copper oxide, Catalytic Activity, Nano-Composites, NO Reduction, Gas-Phase.

INTRODUCTION

The detrimental effects of NO_x (NO and NO_2) have been well documented and include the formations of photochemical smog and acid rain as well as direct negative effects on the human respiratory system [1]. NO_x has been formed in all combustion processes from the high temperature reactions between N_2 and O_2 [2]. The reduction of nitric oxide in gas exhaust streams, from combustion processes, containing a large excess of O_2 remains one of the most intensively studied areas of heterogeneous catalysis [3-5]. The developments of an active selective and stable catalyst have been found immediate application in the treatment of exhausts from lean burn gasoline and diesel engines. One very successful technique for the removal of NO_x has been used commercially in the treatment of exhaust gases of stationary power generation plants [6-8]. This involves the selective catalytic reduction of NO_x with an added reducing agent, i.e. NH_3 . The NH_3 selectively has been reacted with the NO_x component of a gas stream without reacting with the O_2 (which is present in a large excess) [9]. The catalysts used in these reactions are generally either zeolitic- or vanadia-based [10]. For obvious reasons it would not be possible to use NH_3 as a selective reductant on a lean-burn gasoline or diesel powered car, i.e. it is corrosive, toxic, a primary and secondary pollutant and, due to its being a gas, difficult to handle requiring pressurized safety systems and very accurate dosage control mechanisms [11-13]. This investigation was found that oxide supported CuO catalysts show activity in the SCR- NH_3 reaction with the level of activity being related to the support. Distinct experiments of base adsorption and thermal desorption evidenced the higher amount and higher acid strength for these catalysts compared together [14-15]. The dispersion of CuO, in an amount less of 5 wt. % in copper, lead to an appreciable decrease of surface area if compared with the surface area value of the support. However, the final catalysts were maintained appreciable surfaces. The support coverage by copper oxide can be completed and an estimated theoretical coverage of 10-12 wt. % for CuO@SiO_2 can be calculated. The recent investigation was devoted to the systematic reactivity study of NO_x reduction on dispersed copper oxide nano-catalysts over silica supports, in order to determine the ability of these materials to convert nitrogen oxides into harmless species at different temperatures. The host matrices were extensively embedded with copper oxide that was produced with one distinct concentration about 10-12 wt %.

The characterization of the catalyst was examined by TEM, BET and TPR methods at different temperatures [16-18]. Also, FTIR spectra confirm the convert NO_x reduction to harmless species.

2.EXPERIMENTAL DETAILS

In this investigation, the raw materials consist of tetraethyl orthosilicate (TEOS) (Fluka, 98%), ethanol absolute (EtOH) (Merck), copper nitrate tri-hydrated ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (Merck), copper sulfate pentad-hydrated ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were as the initial solution, nitric acid (HNO_3) (Merck, 65%) were used as catalysts, with the mentioned specification.

Nano-composites were prepared from TEOS (tetraethyl-orthosilicate), ethanol and de-ionized (DI) water in a new total molar ratio of $\text{TEOS}:\text{EtOH}:\text{H}_2\text{O}=1:4:11.7$ with HNO_3 as catalyst. Copper nitrate tri-hydrated (10 wt %) and copper sulfate pentad-hydrated were added to the starting solution during preparation. Three catalysts studied in this work were prepared starting from silica supports onto which the CuO phase was doped. The catalysts were synthesized by the sol-gel route and the CuO dispersion was performed by this method starting from copper nitrate precursor. Details on the adopted dispersion methodology can be found in refs [19-20]. The obtained powders were labeled as SG-400, SG-600 and SG-800 were dried at 110 °C for 3 hours and eventually calcite at 400, 600, and 800°C for 1.5 hours. The main characteristics of the supports and catalysts were collected in table 1. Loaded catalysts of 10% were prepared using conventional incipient wetness impregnation using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ precursors. They were then dried (100 °C)



and calcite (400, 600, and 800 °C) with rate of 50°C/h for 1.5-2 hours. The nano-composites (25 mg) were held in a tubular quartz reactor using plugs of quartz wool. The reactants were blended using electronic mass flow controllers from cylinders of 1% NO and 1% NH₃ in He (BOC Special Gases), O₂ and He (BOC) to give a reaction mixture of [NO]=1000 ppm, [NH₃]=1000 ppm, [H₂O]=12% and [O₂]=13% in a total flow of 100 ml/min. H₂O were introduced into a heated zone before the reactor from a calibrated syringe driver. The reactions (SCR-NH₃) were studied under temperature-programmed conditions with a ramp rate of 108°C/min between 120 and 500°C. Levels of NO were continuously analyzed, following suitable dilution, using a Monitor Labs Inc. Nitrogen Oxides Analyzer (Model 8840) connected to a PC. The nano-composites were characterized using temperature-programmed reduction (TPR) on an in-house constructed apparatus. The samples were held in a quartz reactor under a flow of 3% H₂/Ar as the temperature of the reactor was ramped between room temperature and 1000°C. Any reduction event was monitored (as a decrease in the H₂ (g) concentration) using a thermal conductivity detector (TCD). Any H₂O produced during the reduction of the catalyst was trapped using a dry ice trap. Unfortunately, H₂S produced from reduction of sulfate groups on the catalyst was not trapped by the dry ice and thus the formation of H₂S was also detected by the TCD. The catalyst mass was 25 mg, the flow rate of H₂/Ar, 22 ml/min and temperature of the furnace ramped at a rate of 8.6°C/min. Catalyst acidity, and catalyst interaction with NH₃ was probed using temperature-programmed desorption of NH₃. The catalyst (25 mg) was dosed with NH₃ (2860 ppm) at 110°C for 30 min. The NH₃ was then removed from the stream and the catalyst cooled to 50°C in a flow of He (70 ml/min). It is held at this temperature for 20 min and then the temperature was ramped from 50 to 550 °C at a ramp rate of 10°C/min.

A Transmission Electron Microscope (TEM) Em208S series, (Phillips Company) operating at 100 kV was used for this investigation. The dry samples were ground suspended in dry cyclohexane and sonicated for 30 minutes. Then the solutions were allowed to settle and a droplet of the resulting supernatant was placed on a holey carbon film and dried [21].

The porosities of the samples were analyzed by nitrogen adsorption/desorption measurements fitted to a BET isotherm using an autosorb instrument (Quanta-chrome, Nova 1200). The samples were pre-treated for 3 hours under vacuum at 100°C (for the sample dried at 100°C) and at 200°C (for samples treated at 400, 800 and 1000°C). Gaseous nitrogen was used with a 5 hours adsorption/desorption cycle.

Temperature-Programmed Reduction (TPR) was used to investigate the availability of copper species for the reaction with gas-phase molecules. The sol-gel samples were used for the TPR directly after the thermal treatment with no pre-activation. For TPR experiments, 20 mg samples in a quartz tube under H₂ (8%)/N₂ flow were heated at 10°C. min⁻¹ up to 700°C and the H₂ consumption monitored by a thermal conductivity detector (TCD).

The acidity of solution (pH) was measured by Omega pH-meter, model 744.

The condensation and annealing of the samples were done in a heat furnace with high thermal capacity (1500°C).

3. RESULTS AND DISCUSSION

The effect of metal oxide such as V₂O₅ catalysts for the NO reduction with NH₃ at low temperatures (150-250°C) was studied using a transient method. The results show that the presence of SO₂ in the reaction stream can significantly promote catalytic activity, which is largely conditioned by V₂O₅ loading and reaction temperature [22].

The microstructure of the xerogel was examined by TEM. Powder samples with 10-12 wt % copper after ambient drying and thermal treatment at 400°C in air for 1 hour were objected to TEM using bright field, and the resulted image was shown in Fig. 1. No crystalline species were detected without thermal treatment, and bright field images show a typical amorphous xerogel. After heating at 400°C, copper species start to segregate. This figure confirms the formation of average size of about 5 nm. This process was completely depended on the effects of thermal treatment and copper source. These metallic nano-composites have a structure with excellent stability and reproducibility [23].

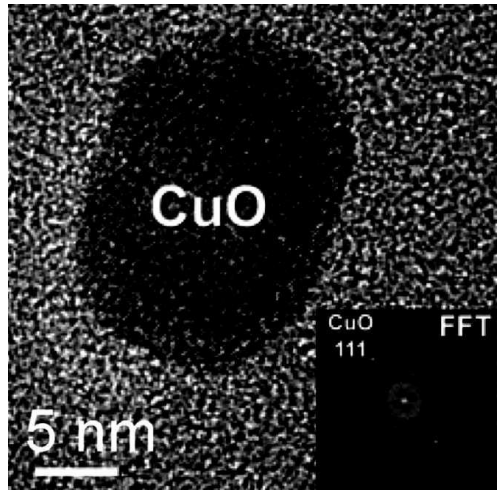


Figure 1. The TEM micrograph of CuO@SiO₂ nano-composite at 400°C.

It has been reported that interaction of support and metal was performed by hydrogen atom i.e. metal or metal oxide interacts with hydroxyl groups. The obtained data were shown that the treatment at 400°C produced the largest surface area, pore size radius with the lowest density. These results indicate the loss of volatile compounds from the porous structure. Once the volatile compounds were eliminated from the network, an increase occurs in the porosity and the gas pore interfaces. Despite this weight loss, a little shrinkage was observed for the material treated at 400°C, resulting to density decrease.

Sample	Surface area (m ² g ⁻¹)	Pore radius (Å)	ρ_{pic} (g cm ⁻³)	V_p (cm ³ g ⁻¹)
CuO100-400	38% +	41.6% +	2.7% -	211.7% +
CuO400-600	21% +	22.3% +	4.3% +	11.6% +
CuO600-800	61.6% -	35.7% -	1.3% +	79% -
CuO800-1000	95% -	64.3% -	32.4% +	92.3% -

TABLE 1. Thermal treatment effects on the surface area, porosity and density of CuO@Silica.

It is interesting for the sample treated at 400°C, which the surface area increases by 38% (from 254 to 351 m²·g⁻¹), whereas the pore volume shows a much more pronounced increase of 211.7% (from 196 to 611 cm³·g⁻¹).

TABLE 2. Variations percent of textural properties to thermal treatment.

Sample	T(°C)	Surface area (m ² g ⁻¹)	Pore radius (Å)	ρ_{pic} (g cm ⁻³)	V_p (cm ³ g ⁻¹)
CuO100	100	254	12	0.72	196
CuO400	400	351	17	0.7	611
CuO600	600	425.1	21.8	0.73	682
CuO800	800	163	14	0.74	143
CuO1000	1000	8	5	0.98	11

For the sample treated at 800°C, the surface area decreases of 53.5%, whereas the pore volume shows reduction of 76.6%. Also, for the sample treated at 1000°C, a surface area decrement of 95% was observed, whereas the pore volume shows a reduction of 92.3% and porosity decrease of 64.3% (from 14 to 5 Å). Although, this effect is not clear, it was related to the size and shape of micro, meso and macro-porous, which modify as the sample was treated at different temperatures [23]. For the higher temperatures (800 and 1000°C) the surface area and porosity strongly decrease due to densification process. The results were presented a significant contribution of micro-porous in the material treated at 100 and 400°C. For higher thermal treatment, the surface area decreases due to the presence of micro and meso-porous, but the contribution of the meso-porous area in the total surface progressively increases [24]. Thermal Program Reduction (TPR) experiments were shown the reduction of copper species to Cu⁰ by H₂. Both Cu⁺² and Cu⁺¹ ions were reduced



directly in a single step to form of Cu^0 according to the reactions $\text{Cu}^{+2} \rightarrow \text{Cu}^0$ and $\text{Cu}^{+1} \rightarrow \text{Cu}^0$. TPR analyses of the samples treated at different temperatures were presented in the Fig. 2. The TPR profile of the sample Cu100 shows three hydrogen consumption peaks; a large peak at 325°C (1), two minor ones at 280 (2) and 245°C (3). For sample Cu400, the TPR profile was shifted at ~25°C to lower temperatures. The largest peak was observed for the sample Cu400 at 290°C (1) was much smaller and the other peaks at 255 (2) and 220°C (3) increased in intensity. These results indicate that the peak (1) was related to the reduction of $\text{Cu}(\text{NO}_3)_2$ and the peaks (2) and (3) are due to the reduction of copper oxides. When the sample was treated at 800 °C, TPR profiles were shifted back to higher temperatures and peak (1) related to $\text{Cu}(\text{NO}_3)_2$ was absent, whereas peaks (2) and (3) related to copper oxides, increase strongly in intensity. At 1000°C, TPR profiles present that the peaks (2) and (3) were mixed together and form a broad peak.

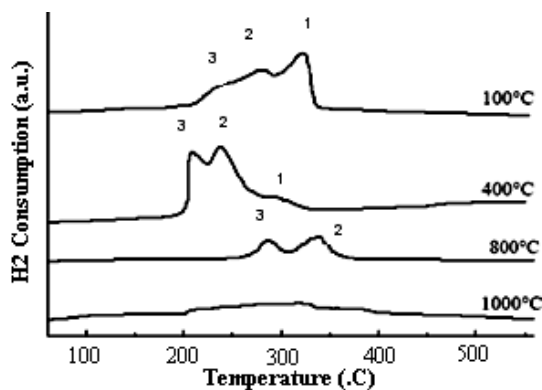


Figure. 2 The TPR profiles of $\text{Cu}(\text{NO}_3)_2\text{-SiO}_2$ samples treated at 100, 400, 800 and 1000°C.

TABLE 3. TPR of H_2 consumption for CuO@SiO_2 .

Thermal Treatment temperature (°C)	H_2 consumption (mol g^{-1})	Relative H_2 consumption (%)
100	650	100
400	650	100
800	300	46
1000	100	15

It can also be observed that the hydrogen consumption decreases as treatment temperature increases, according to the results indicated in Table 3. The samples annealed at 800 and 1000°C only have 46% and 15% of amount of copper species available for reduction, in comparison to the samples annealed at 100 and 400°C, respectively. These results could be related to the reduction of copper ions by the organic compounds presented in the silica matrix during the thermal treatment. Moreover, all thermal treatments were carried out in air atmosphere and a reduced copper form such as Cu^0 would be unlikely. To explain the decrease in TPR of H_2 consumption, one can envisage that treatment at temperatures higher than 800°C, the densification process with sintering and closing of the pores may lead to an entrapment of copper species in the vitreous silica matrix. The entrapped copper species will not be available on the surface for the reaction with H_2 during TPR experiments [25]. In this investigation, has found that oxide supported CuO catalysts show activity in the SCR- NH_3 reaction with the level of activity being related to the support upon which CuO was dispersed as well as the precursor (ex- NO_3^- or ex- SO_4^{2-}) from which the CuO was manufactured. Sulfate species remained on the catalyst surface following calcinations while the nitrate precursors were removed by calcinations and it is thought that sulfur modifies the activity through altering the acidity of the material as well as in a simple site blocking manner. Generally the catalysts were active between 250 and 400°C with activity decreasing at higher temperatures due to competition with the unselective NH_3 oxidation reaction [26]. Residual sulfates were contained several effects, i.e. increasing the temperature at which the SCR- NH_3 reaction gave a maximum conversion and poisoning the catalyst reactivity for the unselective NH_3 combustion reaction at higher temperatures. In the current work the activity of these catalysts were characterized with using a variety of temperature programmed techniques. Figure 3 shows the combined TPR profiles from the three sets of catalysts. The lower profiles relate to the SiO_2 -supported materials. There is only one peak seen in these profiles at 285°C. The peak is far more intense in the case of the ex- SO_4^{2-} material than from ex- NO_3^- catalyst. In the case of the ex- NO_3^- catalyst the peak is due to the single reduction of CuO to $\text{Cu}+\text{H}_2\text{O}$. This was occurred at a lower temperature than that at which bulk CuO was reduced (360°C) and the reason for this decreased temperature of reduction is probably a CuO particle size effect [27].

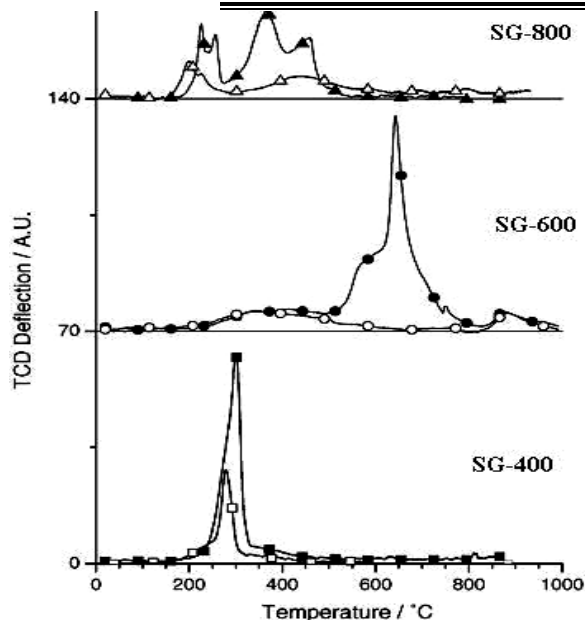


Figure. 3- Displaced temperature-programmed reduction profiles from each nano-composites at 400, 600, and 800 °C temperatures (Open symbols ex-NO₃⁻, filled symbols ex-SO₄²⁻).

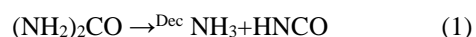
The increased area of the peak arising from the ex-SO₄²⁻ material is due to the reduction of CuO and the concomitant reduction of SO₄²⁻ to H₂S and H₂O (and also possibly releasing SO₂). This affects the TCD signal in two ways, firstly removing more H₂ and secondly exposing it to H₂S causes it is to register a further imbalance. The fact that the SO₄²⁻ reduction peak and the CuO reduction peak were occurred at the same temperature indicates that the sulfate and CuO species were presented in closely related agglomerates on the surface. This is not an unfeasible proposition as it can be reported that sulfate species are not stable on a SiO₂ surface and

thus the residual sulfurs presented on the catalyst must be in some way were related to the CuO. Once the CuO material was reduced (to Cu+H₂O) the bonds anchoring the SO₄²⁻ to the surface were removed and the sulfate was lost (either as SO₂ or following reduction as H₂S). The middle set of profiles in Fig. 3 shows the reduction of the SG-600 catalysts. The ex-NO₃⁻ materials show two peaks. There is a very broad peak between 200 and 600 °C, which was related to the reduction of CuO. The broadness of the peak suggests that there is a wide distribution of CuO particle sizes on the material. There is another peak seen at higher temperature (850–950 °C), which has previously been related to the reduction of the surface [28]. Both of these peaks are also seen (with exactly the same profiles over the ex-SO₄²⁻ catalyst. This suggests that presence of the SO₄²⁻ does not alter the CuO particle size distribution on the support or the reducible characteristics of the support itself. There is another large feature of the ex-SO₄²⁻ profile that is seen between 540 and 750 °C. This was related to the reduction of SO₄²⁻ species on the surface. This fact that these reduction peaks take place at far higher temperatures than the reduction of most of the supported CuO (200–600 °C) suggests that SO₄²⁻ is stable on the support at locations remote from the Cu particles (since it remains on the surface after CuO was reduced to Cu₀). Finally, the upper two profiles relate to the reduction of SG-800 supported materials. These two peaks were seen over the ex-NO₃⁻ sample, one peaking at 225 °C and one at 450 °C. Literature suggests that the first peak is due to the reduction of CuO to Cu (at a lower temperature than the reduction of “bulk” CuO—again probably due to particle size effects). The second peak was previously ascribed to the reduction of matrix. This reduction in the absence of metallic species on the surface was reported to take place at 630 °C and the reason for the lower temperature in the presence of Cu is reportedly due to the spill over of hydrogen from metallic particles to the oxide surface. With regard to the ex-SO₄²⁻ material the peaks are generally larger than those from the ex-NO₃⁻ catalyst (for the reasons discussed above). On this material there are still two general areas of reduction (200–280 °C and 300–500 °C). However, now each of these peaks is split into two, showing complex behavior related to the reduction of the CuO, the matrix and the SO₄²⁻ components. If we assume that the lower temperature series of peaks is still related to CuO reduction we can suggest that there is SO₄²⁻ associated with the CuO on the surface (due to the higher intensity and split nature of the peak). The splitting of the higher temperature peak is due to the reduction of matrix (as before) and the reduction of SO₄²⁻ deposited upon the matrix. In the absence of CuO(s) the reduction of SO₄²⁻ on a support surface takes place at T > 600 °C. We assume that this temperature is again lowered here due to spill over of H-species from Cu.

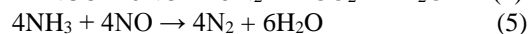
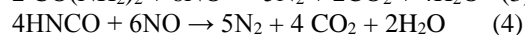
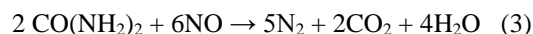


Regeneration of nitrate ions from nuclear effluents

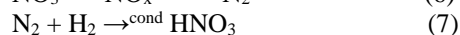
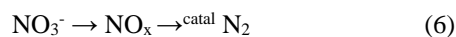
These CuO@SiO₂ nano-composites are very active in high volume space and have high selectivity for N-containing species in gas-phase. This investigation presents that NH₃ is very effective for NO reduction, but unfortunately, maintains and access are very difficult, but its application is very necessary. The needed NH₃ were produced by hydrolysis and decomposition of urea solution according the following reactions;



Urea is the best source for NH₃, because urea solution is a non-toxic material and transportation is easy as aquatic solutions. In this method, NO gas-phase can be reduced with NH₃, also urea and its decomposition produce a bi-product HNCO.



Nitrogen oxide was produced with solving nuclear fuel in nitric acid and de-nitration of metals nitrates. The processing of nitric acid were performed, also effluents processing were done from metals nitrate ions of nuclear industrial effluents by CuO@SiO₂ nano-composites. Metals nitrate ions regeneration of nuclear industrial was performed by thermal decomposition. In this processing, nitrate ions in solution convert to NO_x and then NO_x vapors in neighbor catalyst convert to nitrogen gas and second step to nitric acid. The produced nitric acid can be used again in nuclear industrials.



There are the nitrate ions in nuclear industrials containing Na, K, NH₄, Cu, and Mg metals nitrates. This processing consist 2 steps; at first, in reactor vessel, a thermo mechanical attachment were done between solution and gas flows. Then metal nitrates solution were distributed to micro drops form. The thermal flows are in higher temperatures of nitrate decomposition temperatures in solution (usually above of 500°C). They have a mechanical energy for decomposing the produced particles. Immediately, nitrate decompositions were accomplished with produce of NO_x vapors which reduced to N₂ with CuO@SiO₂ nano-catalyst. At second, NO_x gas can be converted to nitric acid by condensation and absorption in aquatic solutions.

The nitric acid can be injected again to nuclear industrials, and applied a; for solving Uranium concentrators produced from purification processing of Uranium ores and b; for solving nuclear fuel tabs before using in nuclear reactors.

In the project operator view, this processing is very difficult and for operation and we need to complex accessory instruments. The project operators plan the schematic patterns of chemical micro-reactor for regeneration nitrate ions from nuclear industrial effluents in second project phase. This project has improved about 70 % with manufacturing and characterization of CuO@SiO₂ nano-composites as catalyst for NO₂ decomposition, CO oxidation, NO_x reduction and study of conversion NO₃⁻ to HNO₃ in nuclear industrials effluents.

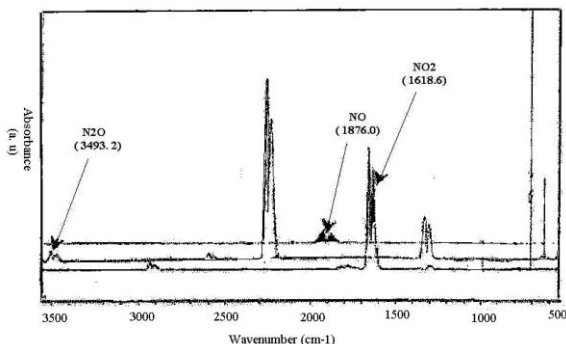


Figure 4. FTIR spectrum of the N-containing species studied in the various reactions as reactants and/or reaction products

The fed and vented gases from the reactor alternatively were flowed through a gas cell (multiple reflection gas cells with 2.4 m path length) in the beam of the FTIR spectrometer. The measurements were carried out at 0.50 cm^{-1} resolution, with accumulation of 19 scans per spectrum. NO (1876.0 cm^{-1}), N₂O (3493.2 cm^{-1}), and NO₂ (1618.6 cm^{-1}) for the N-containing species were quantified by the intensity of selected absorbance lines in Fig. 4. The copper oxide contents have been affected on the catalytic activity of CuO@SiO₂ nano-composites. The obtained results were presented that 10 % weight percent samples have highest surface area and pore volume with the lowest density and particle size. These nano-compounds are suitable for catalytic conversion at NO_x reduction reactions.

4. CONCLUSIONS

The evolution of the copper species moves from copper nitrate and copper sulfate to copper oxide species by sol-gel route and thermal treatment. The annealing processing was performed at 400, 600, and 800°C. The obtained samples were studied at these temperatures of NO_x reduction catalytic activities. The structural properties were analyzed by TEM micrographs and confirm the formation of colloidal particles of copper oxide about 5 nm. Also, The TPR experiments show the reduction of copper species to Cu⁰ by H₂. Both Cu⁺² and Cu⁺¹ ion were reduced directly in a single step to form of Cu⁰ according to the reactions $\text{Cu}^{+2} \rightarrow \text{Cu}^0$ and $\text{Cu}^{+1} \rightarrow \text{Cu}^0$. Also, these experiments present relation between H₂ consumption at diverse temperatures. In the author view, there is a correlation between the existence of copper oxide particles embedded into the silica matrix, and the effects of thermal treatment. These effects might be influenced to the interaction between the guest particles and the matrix host. According to this study, the exact composition of nano-composites depends on the annealing temperatures and the choice of appropriate copper source and procedure of nano-particles. Also, the results were presented the NH₃ selective catalytic reduction reactivity of NO reduction on dispersed copper oxide nano-catalysts into silica supports, in order to determine the ability of these materials to convert nitrogen oxides into harmless species at different temperatures.

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