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SIMULTANEOUS REMOVAL OF NO AND SO_2 FROM COMBUSTION FLUE GASES USING SUPPORTED COPPER OXIDE CATALYSTS

O.A. BEREKETIDOU
N.D. CHARISIOU
M.A. GOULA*

Technological Educational Institute of Western Macedonia (TEI WM)
Pollution Control Technologies Department (PCT)
Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC)
Koila, Kozani, 50 100, Greece

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*to whom all correspondence should be addressed:
e-mail: mgoula@kozani.teikoz.gr

ABSTRACT

Nitrogen oxide (NO_x) and sulphur dioxide (SO_2) emissions produced by the combustion of fuel in stationary sources, such as power stations, industrial heaters or cogeneration plants, cause significant environmental problems. Selective catalytic reduction (SCR) is a well established process for the control of NO_x emissions mainly due to its efficiency, selectivity and economics. High removal efficiencies for both NO_x and SO_2 can be achieved with the use of copper oxide catalysts, as they act as sorbents for the latter - forming copper sulfate - and catalyze the reduction of the former - to N_2, in the presence of NH_3. An added advantage is that these catalysts are relatively easy to be regenerated under reducing conditions.

This study examines the deactivation and regeneration procedures of copper oxide catalysts/sorbents that are supported on Al_2O_3, SiO_2, CeO_2-Al_2O_3, in the presence of SO_2 and identifies the appropriate conditions for the simultaneous removal of NO and SO_2. The results obtained indicate that copper oxide supported on alumina, ceria-alumina and silica carriers, can be used as effective catalysts for the simultaneous removal of NO and SO_2. Furthermore, they can be easily regenerated with a gas mixture of 1 % NH_3/Ar at an optimum temperature of 673 K and they retain their initial activity. Thus, the use of regenerative fixed bed catalytic reactor appears as one of the most promising technologies however, further research focusing in new catalytic materials performance is necessary.

KEYWORDS: Selective Catalytic Reduction (SCR), Copper Catalysts, NO_x Emissions, Regenerative SO_2 Adsorption.

INTRODUCTION

In the last decades, air pollution has moved at the top of the international political agenda due to its adverse environmental and health effects. The long-range transport of pollutants across country borders has made necessary the extensive cooperation of both the scientific and policy-making communities.

A major cause of concern is the NO_x and SO_2 emissions, which result from the process of fuel combustion in stationary sources (power stations, industrial heaters and cogeneration plants). Typically, NO_x and SO_x in flue gases consist of over 90-95 % of nitric oxide (NO) and more than 98 % of sulfur dioxide (SO_2) (Popp, 2006). NO_x is responsible for the formation of ozone in the troposphere, the production of acid deposition and photochemical smog, while its adverse health effects on humans include a variety of respiratory diseases. Sulphur oxides ($SO_x = SO_2 + SO_3$) are responsible for the formation of acid rain and the destruction of the ozone layer. Thus, the reduction of NO_x and SO_x emissions has become the focus of air pollution control (Zhao *et al.*, 2008; Cheng *et al.*, 2008).

Selective catalytic reduction (SCR) is a well established process that is used for the control of NO_x emissions mainly due to its efficiency and selectivity. A major constraint is the narrow operating range of the SCR catalysts (i.e., 473-700K). However, post combustion NO_x removal processes such as selective catalytic and non-catalytic reduction are relatively expensive and are economically feasible only for large-scale combusters. Arguably, the simultaneous removal of SO_2 and NO_x, using a regenerable solid catalyst sorbent, will constitute an important improvement over the use of separate processes for the removal of these two pollutants, as it will eliminate several shortcomings.

Copper oxide catalysts on various supports, such as CuO/ZrO_2, $CuO/\gamma\text{-}Al_2O_3$, CuO/SiO_2 and CuO/TiO_2 exhibit high performance in low-temperature NH_3-SCR. The activity and selectivity of copper-based catalysts are determined to a great extent by the texture and dispersion state of CuO_x species, which are influenced by the surface state of supports (Li *et al*., 2011). CuO/Al_2O_3 is an important sorbent-catalyst for simultaneous SO_2 and NO_x removal from flue gas (Xie *et al*., 2004a). During SO_2 removal, CuO reacts with SO_2 in the presence of O_2 to form $CuSO_4$, whereas some of the Al_2O_3 may also react with SO_2 to form $Al_2(SO_4)_3$ (Zhao *et al.*, 2007). Upon saturation of the CuO/Al_2O_3 by SO_2, it should be subjected to a regeneration treatment to convert $CuSO_4$ back to CuO (elementary Cu in some case) and gaseous SO_2 by a reducing gas such as H_2, NH_3, or CO. The literature on sulfation, regeneration, and effect of SO_2 on NO_x removal of CuO/Al_2O_3 catalyst sorbents indicates that SO_2 has varied effects on NO_x removal in different temperature ranges (Xie *et al.*, 2004b). Specifically, it promotes SCR activity in the range of 623–723K, but reduces it at temperatures below 573K (Zhao *et al.*, 2007). By using copper catalysts/sorbents, high removal efficiencies can be achieved, as they act both as sorbents for SO_2 to form copper sulfate and also catalyze the reduction of NO_x to N_2 in the presence of NH_3. The development of practical regeneration processes, such as oxidation-regeneration cycles have opened novel applications for catalytic materials which can integrate dual functions (Guo *et al.*, 2007; Liu *et al.,* 2010).

Other studies consider *cerium oxide* as an alternate sorbent to CuO as ceria improves the resistance of the alumina support to thermal sintering (Hedges *et al*., 1992). The wide application of cerium oxide either as a promoter or as an active catalyst is due to its unique redox and acid–base properties. Lattice oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed during the redox shift between Ce^{3+} and Ce^{4+} under oxidizing and reducing conditions, respectively (Xu *et al*., 2008).

There are a few studies, which indicate that ceria possesses sufficient activity and selectivity as a catalyst for the reduction of NO with NH_3 at relatively *high* temperatures used for SO_2 removal (Akyurtlu *et al*., 1999; Bereketidou *et al.*, 2009; Gao *et al.*, 2010).

Silica-supported CuO catalysts have been tested for their activity and selectivity with respect to catalytic reduction of nitric oxide by ammonia (Kiel *et al*., 1992). All catalyst samples investigated show a high selectivity towards the reaction of NO with NH_3 and O_2, to N_2 and H_2O, irrespective of the degree of sulphation. However, the selectivity of the partially sulphated silica supported CuO catalyst towards the catalytic reduction is maintained up to a temperature of about 648K, which enables application of the sorbent-catalyst in a process for simultaneous removal of SO_2, and NO_x (Kiel *et al.*, 1992).

In the present work, the effect of SO_2 on selective catalytic reduction (SCR) of NO by NH_3 over CuO/Al_2O_3, CuO/SiO_2 and $CuO/CeO_2\text{-}Al_2O_3$ catalyst sorbents has been investigated. The present study aimed at examining the simultaneous removal of SO_2 and NO using fresh and regenerated CuO catalyst sorbents at temperature ranges of 423-623 K. The tolerance to SO_2 presence and the effectiveness of the regeneration process to CuO supported on alumina, ceria-alumina and silica catalysts were also studied.

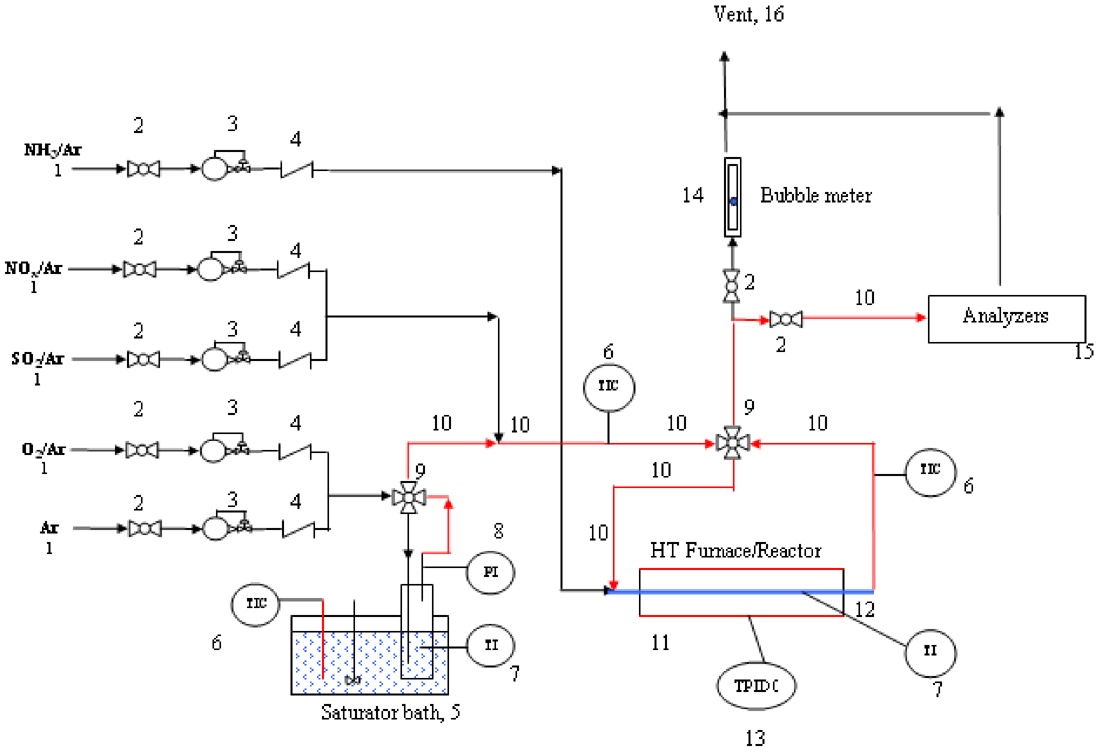
EXPERIMENTAL METHODS

As supporting materials, $\gamma\text{-}Al_20_3$ (AkZO, $S_{BET} = 281\ m^2\ g^{-1}$) and SiO_2 (Engelhard, $S_{BET} = 145\ m^2\ g^{-1}$) particles (350-500 μm) were used. Prior use, they were dried at 383 K overnight, and calcined at 873 K for 5h in an air furnace. Supporting $CeO_2\text{-}Al_2O_3$ materials were prepared by impregnating γ-alumina particles with aqueous solutions of $CeN_3O_9\ 6H_2O$. Catalysts were prepared by the dry impregnation technique, using $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solutions with the appropriate concentration, in order to obtain a final copper (Cu) content equal to 8 % wt. All the catalyst samples were air-dried overnight and calcined at 873 K for 5 h.

Elemental analysis was performed using the Inductively Coupled Plasma Atomic Emission Spectroscopy technique (ICP-AES - Perkin-Elmer Optima 4300DV) in order to determine the actual copper content of the catalyst samples. The specific surface area (SSA) of the supports was obtained with BET measurement (Micromeretics Tristar Apparatus with Micromeretics VacPrep 061 Sample Degas System). Catalyst samples were also characterized by XRD (Siemens D500 diffractometer) for the determination of the crystalline phases.

The gas flow system used for conducting catalytic measurements at 1atm total pressure consisted of a mass flow measuring and control system, a mixing chamber, a fixed bed catalytic reactor and Buhler NO_x, SO_2, O_2 analysers. The inlet gas composition was 625 ppm NO, 625 ppm NH_3, 1600 ppm SO_2 (when used), 5.5 vol % O_2, 3 vol % H_2O and balance Ar, simulating a flue stack gas. 2.0 g of sample was placed between two plugs of quartz wool held in the reactor, which was heated by an electrical furnace. In all the runs, the total flow rate was controlled at 3 L min^{-1}, which corresponds to a space velocity (GHSV) of 90,000 mL g^{-1} h^{-1}. The flow diagram of the system used for catalytic activity measurements is presented in Figure 1.

The catalyst bed in the reactor was preheated in Ar (500 mL min^{-1}) at 673 K for 1h and then was cooled down to the reaction temperature. The effect of the reaction temperature, time on stream and the regeneration capability using NH_3 as regenerating agent, were studied. Moreover, the influence of CeO_2 content of the supporting materials to the overall catalytic performance has also been investigated.



1. Gas Cylinders
2. On-Off Valves
3. Mass flow controllers
4. Check Valves
5. Saturator Bath
6. Temperature Indicator Controller
7. Temperature indicator
8. Pressure Indicator
9. 4-way valve
10. Heating line
11. Furnace
12. Reactor
13. TPIDC
14. Bubble Meter
15. Analyzers
16. Vent

Figure 1. Flow Diagram of the fixed-bed reactor system for catalyst testing

RESULTS AND DISCUSSION

Characterization results

The specific surface areas and the crystalline phases of the supporting materials being calcined at 873 K for 5 h are presented in Table 1. As can be seen, higher CeO_2 loading (20 wt % CeO_2) decrease significantly the supporting material surface area. The XRD patterns of the supports exhibited the diffraction peaks of crystalline γ-aluminum oxide (γ-Al_2O_3), silicon oxide (SiO_2) and cerianite (CeO_2).

The XRD patterns of the supported catalysts depict that copper has been present as *CuO* crystalline phase on their surface, while elemental analysis reveal that copper loading is approximately 8 wt % for all of the samples.

Table 1. Characterization results of the supporting material

Supporting material	Specific surface area (m^2 g^{-1})	Crystalline phases (XRD)
γ-Al_2O_3	239	γ-Al_2O_3
SiO_2	108	silicon oxide-christobalite
10 % Ce-A	207	γ-Al_2O_3, cerianite
20 % Ce-A	185	γ -Al_2O_3, cerianite

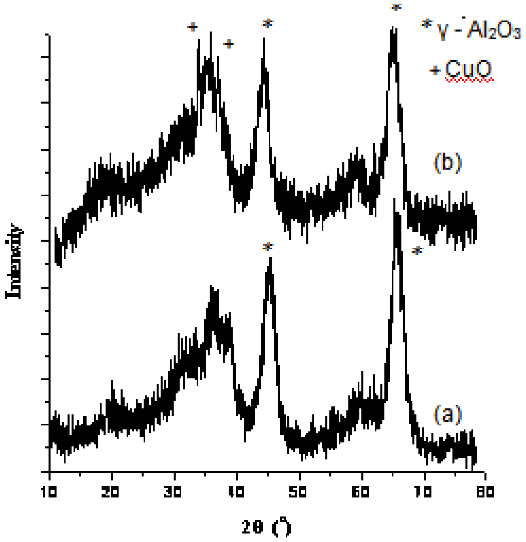


Figure 2. XRD pattern of (a) Al_2O_3 and (b) CuO/Al_2O_3 catalyst sorbent

Crystallite sizes of the CuO/Al_2O_3 of the initial samples pretreated in air at 873 K were determined by the *Scherrer equation*, evaluating the FWHM values with full profile fitting methods and estimated at the range of 20 nm.

Catalytic activity of CuO/Al_2O_3 catalyst

The SCR activity (expressed as a fraction of NO conversion at steady state) of the 8 % CuO/Al_2O_3 at a temperature range of 423–593 K and a space velocity (GHSV) of 90,000 mL g^{-1} h^{-1} in the presence and absence of SO_2 is depicted in Figure 3. In both cases, the catalytic activity increases with increasing temperature, up to 523 K. CuO/Al_2O_3 catalyst reveals high catalytic SCR activity (>90 % NO conversion) for temperature values ranging from 473 to 593K in the absence of SO_2 at the inlet gas. When SO_2 is present, the catalytic SCR activity peaks at 533 K.

The copper on alumina system as a catalyst/sorbent for the removal of SO_2 ($DeSO_x$), acts as an oxidant for SO_2 and as a sorbent to form surface sulfates, and at the same time as a catalyst for the selective reduction of NO with ammonia in the presence of gaseous oxygen, $DeNO_x$ (Centi *et al.*, 1992). After adsorbing SO_2, the CuO in the CuO/Al_2O_3 catalyst-sorbent transfers into $CuSO_4$ and must be regenerated for reusing. The regeneration efficiency is closely related to the subsequent sulphur removal activity and stability of the catalyst-sorbent (Xie *et al.*, 2003). The regeneration of the sulphated samples can be achieved using a reductive treatment with H_2, NH_3 or other reducing

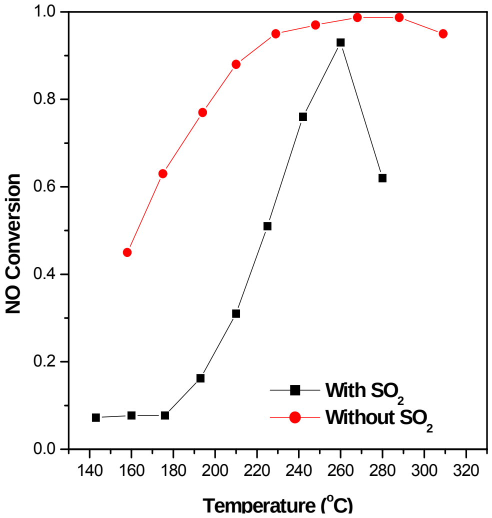


Figure 3. Effect of temperature on NO Conversion in the presence and absence of SO_2 (Experimental Conditions: 625 ppm NO, 625 ppm NH_3, 5.5 vol % O_2, 3 vol % H_2O, catalyst 8 wt % CuO/Al_2O_3, 2 g of catalyst)

agents (Zhao *et al*., 2007; Guo *et al*., 2007). The reaction temperature depends on the reducing agents. The copper formed in the presence of the reducing agent is immediately oxidized to copper oxide upon contact with the flue gas. However, it was found out the problem is more complex than that stated in the literature, which in turn, influences catalyst and reactor design for optimal performances

In the present study, *NH_3* was used to regenerate sulphated CuO/Al_2O_3 catalyst-sorbent. It is likely that NH_3 can be used to effectively regenerate the sulfated CuO/Al_2O_3 catalyst-sorbent at temperatures around 673 K, if so, significant economical advantages can be realized due to regenerating the sulfated CuO/Al_2O_3 at temperatures of desulfurization and elimination of SO_2 conversion units (Xie *et al.,* 2003). The effect of regeneration time at constant regeneration temperature (673K) and NH_3 concentration of 1 % was examined. The experimental results showed that the catalyst activity on NO reduction is lower for regenerated catalysts compared to fresh catalysts. Furthermore, the catalytic activity increases slightly with regeneration time of the used catalyst. It was found out that a regeneration time of 120 min is enough to obtain high activity on NO reduction (approximately 70 %).

The effect of time on stream on NO conversion and SO_2 adsorption over a catalyst 8 wt % CuO/Al_2O_3 for two consecutive cycles at a reaction temperature of 513 K is presented in Figure 4. As can be seen, the catalytic activities for NO reduction, as well as SO_2 removal capacity, are slightly lower over two consecutive cycles. Thus, the SO_2 adsorbed CuO/Al_2O_3 can be regenerated in NH_3 at 673 K to recover its SO_2 removal activity and obtain elementary sulfur.

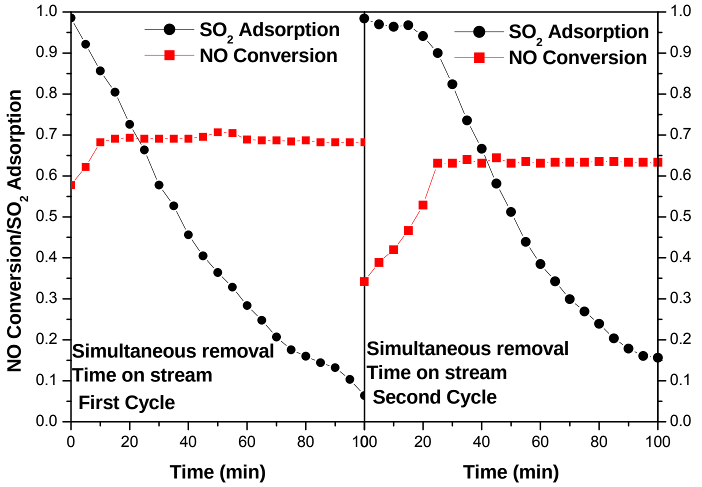


*Figure 4***.** Effect of time on stream on NO conversion and SO_2 adsorption obtained over a 8wt % CuO on alumina for two consecutive cycles (T=513 K)

Catalytic activity of CuO/SiO_2 catalyst

As shown in Figure 5, the CuO/SiO_2 is only highly active at temperatures above 593K (which is in accordance with the literature), while the CuO/Al_2O_3 catalyst (Figure 3) exhibits similar activity at temperatures above 493K.

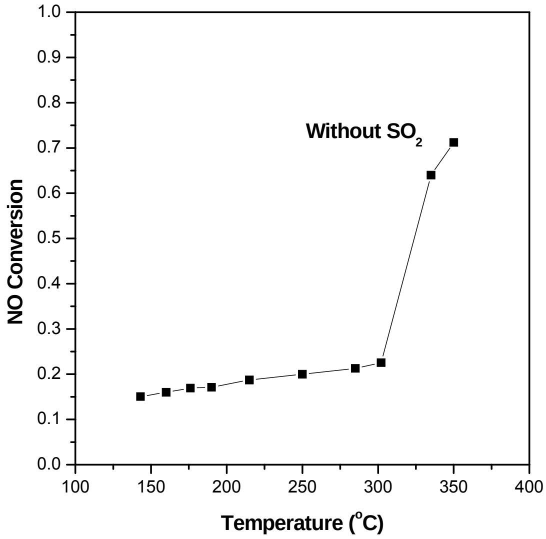


Figure 5. Effect of temperature on NO Conversion in absence of SO_2
(Experimental Conditions: 625 ppm NO, 625 ppm NH_3, 5.5 vol % O_2, 3 vol % H_2O, catalyst 8 wt % CuO/SiO_2, 2 g of catalyst)

Moreover, the CuO/SiO_2 catalyst exhibits higher activity for NO reduction and almost the same SO_2 removal capacity over two consecutive cycles (Figure 6). It was concluded that after 100 min time on stream, the CuO supported on silica catalyst is stable. It should be noted that even after the regeneration treatment, the SO_2 sorption capacity remains about 30 % of the initial one. Furthermore, the SO_2 capture capacity seems to be higher for CuO supported on silica catalyst compared to CuO supported on alumina one, after 100 min time on stream. This leads to the conclusion that silica can be a promising sorbent-catalyst for the simultaneous removal of SO_2 and NO.

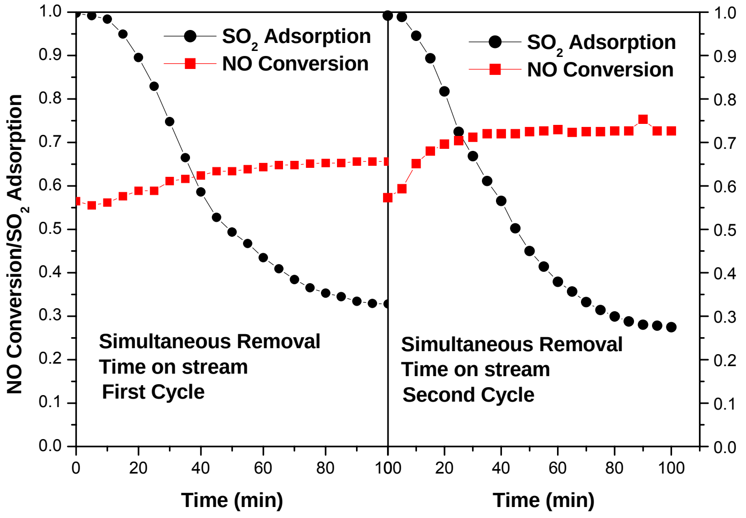


Figure 6. Effect of time on stream on NO conversion and SO_2 adsorption obtained over a 8 wt % CuO on silica for two consecutive cycles (T=623 K)

Catalytic activity of CuO/CeO_2-Al_2O_3 catalysts

Copper oxide (8 % CuO) supported on 10 % CeO_2-Al_2O_3 and 20 % CeO_2-Al_2O_3 catalysts exhibit high values for the NO conversion at temperatures ranging from 493 to 623 K and 573 K to 653 K, respectively, as shown in Figure 7. Increasing the cerium oxide loading in the supporting material, catalysts with improved performance for simultaneous NO and SO_2 removal can be produced. This is attributed to the fact that ceria improves the resistance of the alumina support to thermal sintering and possesses a sufficient activity for the reduction of NO with NH_3 at relatively low temperatures.

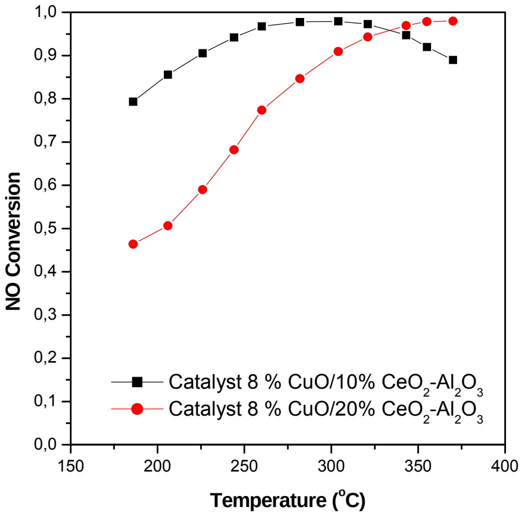


Figure 7. Effect of temperature on NO Conversion in absence of SO_2
(Experimental Conditions: 625 ppm NO, 625 ppm NH_3, 5.5 vol % O_2, 3 vol % H_2O, catalysts 8 wt % CuO/10 % CeO_2-Al_2O_3 and 8 wt % CuO/20 % CeO_2-Al_2O_3 2 g of catalyst)

Nitrogen oxide (NO) conversion and sulphur dioxide (SO_2) adsorption are depicted as a function of time on stream, in Figure 8 & 9. In the case of 8 % CuO supported on 10 % CeO_2-Al_2O_3 catalyst, NO conversion remains constant at 70 % after 100 min time on stream, while the SO_2 adsorption capacity exhibits a sharp decline (Figure 8). In the case of 8 % CuO supported on 20 % CeO_2-Al_2O_3 catalyst, the NO conversion reaches the X_{NO}=1 value at a relatively low temperature (T=613 K), and retains it for about two hours on stream, where the SO_2 adsorption capacity is getting close to zero (Figure 9).

The above observations can be explained by taking into account the sulfation reactions that are assumed to take place on the sorbents consisting of ceria and copper oxide on alumina (Akyurtlu *et al.*, 1999):

$CuO + SO_2 + ½\, O_2 \rightarrow CuSO_4$

$CeO_2 + 1\, ½\, SO_2 + ½\, O_2 \rightarrow ½\, Ce_2(SO_4)_3$

As reported, (Gao *et al*., 2010; Du *et al*., 2012) the formation of surface sulfate will increase the acid number and NH_3 adsorption thus enhancing the SCR activity. In accordance to the literature (Pantazis *et al.,* 2006), copper oxide supported on ceria-alumina catalysts get sulfated ($CuSO_4$ formation), but they don't loose their SCR activity even after 3 hours time on stream.

These results are indicative of the catalyst's high stability for the SCR reaction, despite the relatively high SO_2 concentration (1600 ppm) in the feed. It is also worth noticing that by increasing the cerium oxide loading in the supporting material, a catalyst with improved performance for simultaneous NO and SO_2 removal can be produced.

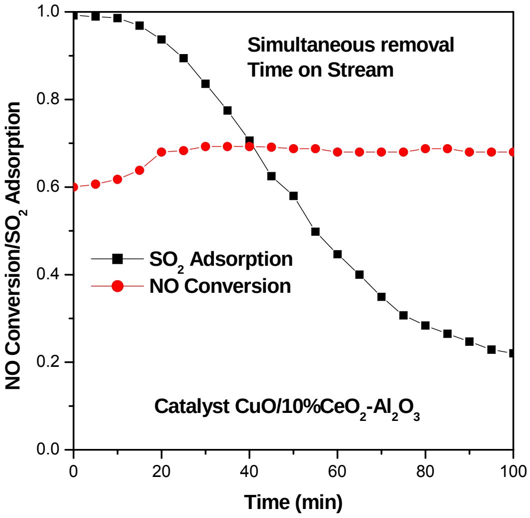


Figure 8. Effect of time on stream on NO conversion and SO_2 adsorption obtained over a 8 wt % CuO on 10 % CeO_2-Al_2O_3 catalyst (T=613 K)

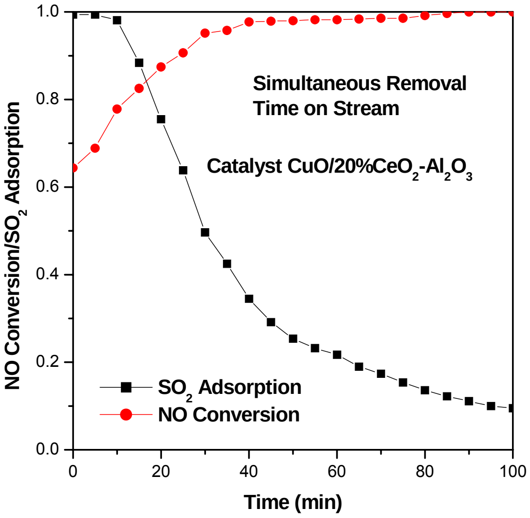


Figure 9. Effect of time on stream on NO conversion and SO_2 adsorption obtained over a 8 wt % CuO on 20 % CeO_2-Al_2O_3 catalyst (T=613 K)

CONCLUSIONS

Supported copper oxide (CuO) catalysts have been tested for their activity towards NO conversion and its adsorption capacity towards SO_2 in the 423-673K temperature range. Catalysts with 8 % copper content supported on 10 % CeO_2-Al_2O_3 and 20 % CeO_2-Al_2O_3 exhibit high values for both NO conversion and SO_2 sorption capacity at temperature values ranging from 493 to 623K and 573 to 653 K, respectively.

CuO/Al_2O_3 catalyst reveals high catalytic activity (> 90 % NO conversion) for temperatures ranging between 473-593 K without SO_2 in the gas stream, while the CuO/SiO_2 catalyst is highly active only for temperature values above 593 K. The CuO/Al_2O_3 catalyst exhibits higher SCR activity than the CuO/SiO_2 one (~ 70 % NO conversion), but SO_2 capture capacity seems to be *higher* for copper supported on silica catalysts compared to alumina supported ones.

Moreover, it was concluded that the catalytic activity on NO reduction is lower for regenerated catalysts compared to the fresh ones, increasing slightly with the regeneration time (120 min is considered adequate so that the highest activity on NO reduction is obtained).

In conclusion, the results obtained indicate that copper oxide supported in alumina, ceria-alumina and silica catalysts can be very effective for the simultaneous SO_2/NO_x removal. Additionally, supported catalysts may be regenerated in 1 % NH_3/Ar at an optimum temperature of 673 K.

In any case, research focused on the development of new catalytic materials with improved performance towards the simultaneous SO_2 and NO removal, is needed. This is particularly urgent given that the development of appropriate techniques for combustion flue gases purification is one of the principal topics in environmental catalysis, particularly after stricter legislation being induced from the EU.

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