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Catalytic activity of dispersed CuO phases towards nitrogen oxides (N_2O, NO, and NO_2)

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Abstract

A systematic reactivity study of N_2O, NO, and NO_2 on highly dispersed CuO phases over modified silica supports (SiO_2–Al_2O_3, SiO_2–TiO_2, and SiO_2–ZrO_2) has been performed. Different reaction paths for the nitrogen oxide species abatement were studied: from direct decomposition (N_2O) to selective reductions by hydrocarbons (N_2O, NO, and NO_2) and oxidation (NO to NO_2). The oxygen concentration, temperature, and contact time, were varied within suitable ranges in order to investigate the activity and in particular the selectivity in the different reactions studied. The support deeply influenced the catalytic properties of the active copper phase. The most acidic supports, SiO_2–Al_2O_3 and SiO_2–ZrO_2, led to a better activity and selectivity of CuO for the reactions of N_2O, NO, and NO_2 reductions and N_2O decomposition than SiO_2–TiO_2. The catalytic results are discussed in terms of actual turnover frequencies starting from the knowledge of the copper dispersion values.

Keywords: Copper catalysts; De-NO_x catalytic activity; Turnover frequencies

1. Introduction

During the last decade, we have assisted to a growing interest for the control of nitrogen oxide emissions (including N_2O, NO, and NO_2 species) from engine exhausts and many anthropogenic activities. Despite the interesting and promising processes and catalytic materials developed, from direct decomposition [1–11] to selective reduction processes using ammonia [12–16], urea [17–20], or hydrocarbons [12,13,21,22–40] as reductants, the problem is far from being completely solved, and it still remains a current environmental concern. Besides NO and NO_2 (collectively known as NO_x), which have been known for a long time to be harmful for the environment, principally due to acid rain formation [13], in the recent years particular interest has been devoted to N_2O. Although N_2O forms naturally only in small quantities via microbial action in soils and oceans, its global concentration in the atmosphere continues to increase faster than at any time in the past due to various anthropogenic activities. The major industrial source of N_2O is the production of nitric acid, which is a key material in the fertilizer industry [9,41]; it is also a co-product in the synthesis of adipic acid [42], caprolactam, glyoxal, and it is also vented by combustion processes of fossil fuels, biomass, and wastes. The continuous accumulation of N_2O is due to its very long lifetime in the atmosphere (about 150 years), where it contributes to the greenhouse effect and ozone layer depletion. The highly negative impact of nitrogen oxide species on the environment and eventually on human life, as well as the prospective more stringent regulations, call for the development of even more efficient and economical systems for N_2O, NO, and NO_2 mitigation.

Among the very large number of catalyst types studied for the reactions of abatement of nitrogen oxides, two major catalytic systems have emerged as promising candidates: copper and iron deposited on various zeolite structures (ZSM-5, MFI, BEA, and beta [2,22–24,39,40,43,44]) and oxides (alumina, zirconia, alumina, titania, and silico–alumina [7,28–32,45]). Iron zeolites have been developed more widely than systems based on oxides. The major problem with iron-containing zeolites is that samples with low iron content display unsatisfactory activity, while samples with high iron content show good activities at too high temperatures [36]. Fe can be stabilized in different forms, ranging from isolated metal ions to large oxide aggregates. Ion-oxo clusters are claimed to be most active for the selective reduction of NO_x [24,46]. As to the copper-containing systems, the first highly active and selective

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systems developed were based on zeolite structures (copper-ion exchanged ZSM-5 zeolite); subsequently, amorphous oxide systems containing small cupric oxide particles (supported CuO_x) and presenting some acidity have been shown to display catalytic behaviour comparable to that of catalysts based on copper–zeolites. These systems are very promising because they possess high mechanical and hydrothermal stability. It is therefore important to further study these systems in order to determine their potential towards the various reactions involving the transformation of nitrogen oxide species.

The present paper is devoted to the systematic reactivity study of N_2O, NO, and NO_2 on dispersed CuO catalysts over modified silica supports (silica–alumina, silica–titania, and silica–zirconia), in order to determine the ability of these materials to convert nitrogen oxides into harmless species (i.e., N_2) by different reaction paths. In this perspective, the N_2O decomposition without hydrocarbon reductant (N_2O-Dec.) and the selective reductions of N_2O (N_2O-SCR), NO (NO-SCR) [30], and NO_2 (NO_2-SCR) by hydrocarbon have been studied. Besides these reactions, the oxidation of NO to NO_2 (NO-Ox.) has also been investigated. This reaction has a two-fold interest: it can be used to convert NO into a species more easily scrubbed in basic medium (NO_2), as an alternative solution for NO abatement, and it can provide information on the possible key role of NO_2 species during the NO-SCR reaction. There is not a unique viewpoint on this subject: some proposed reaction mechanisms put forward the central role of NO_2 formation [36,47–49], while several others hypothesize other key intermediates (i.e., cyanide or nitro-species, etc. [36,50,51]).

For a better comparative interpretation of the obtained results, and in order to evidence the influence of the support on activity and selectivity of the CuO dispersed phase, the present collected data and those already presented in Ref. [30] have been interpreted taking into account the copper dispersion values (surface Cu ratio to the total amount of Cu introduced over the support), which make it possible to calculate the actual turnover frequencies.

2. Experimental

The catalysts studied in this work have been prepared starting from home-made supports (silica–alumina, SA, silica–titania, ST, and silica–zirconia, ST) onto which the CuO phase was deposited. The SA, ST, and SZ supports were synthesized by sol–gel route as described in Refs. [52,53]. The CuO deposition was performed by adsorption method starting from copper acetate precursor. Details on the adopted deposition methodology can be found in Ref. [30]. The obtained powders, labelled as Cu/SA, Cu/ST, and Cu/SZ, were dried at 120 °C for 12 h and eventually calcined at 500 °C for 4 h. The main characteristics of the supports and catalysts are collected in Table 1.

Five different types of catalytic reactions were realized as detailed in Table 2. The reactions were performed in a

Table 1
Characteristics of the catalysts and supports studied in this work

Catalyst	Cu loading		BET surface (m^2/g)	Pore volume (cm^3/g)	Cu dispersion	
	wt.%	$(mmol_{Cu}/g)_{tot}$[a]			Percent	$(mmol_{Cu}/g)_s$[b]
Cu/SA	6.5	1.02	385	0.63	5.0	0.051
Cu/ST	6.3	0.99	230	0.60	12.9	0.128
Cu/SZ	6.9	1.09	313	1.40	10.4	0.113

Support	wt.%	BET surface (m^2/g)	Pore volume (cm^3/g)	Acidity (mequiv/g)	
				$NH_{3,ads}$[c]	PEA_{des}[d]
SA	Al_2O_3, 12.2	777	0.85	0.480	0.503
ST	TiO_2, 13.2	494	0.69	0.307	0.183
SZ	ZrO_2, 14.3	596	1.69	0.374	0.309

[a] $(mmol_{Cu}/g)_{tot}$, total Cu moles deposited on support.

[b] $(mmol_{Cu}/g)_s$, surface Cu moles [57].

[c] Determined at 0.2 Torr of NH_3 coverage by adsorption experiments at 80 °C [53].

[d] Determined by 2-phenylethylamine (PEA) thermodesorption in the temperature range from 360 to 460 °C [52].

Table 2
Studied reactions with the operative conditions applied in this work

Reaction	Feed concentration (ppm)	Temperature (°C)	Contact time (s)
N_2O decomposition ($N_2O + O_2$)	N_2O, 1500; O_2, 15000	450–600	0.36
N_2O SCR ($N_2O + C_2H_4 + O_2$)	N_2O, 1500; C_2H_4, 1500; O_2, 15000	300–600	0.36
NO SCR ($NO + C_2H_4 + O_2$)	NO, 1500; C_2H_4, 1500; O_2, 30000	200–450	0.072–0.36
NO_2 SCR ($NO_2 + C_2H_4 + O_2$)	NO_2, 1500; C_2H_4, 1500; $5000 < O_2 < 15000$	200–500	0.36–0.51
NO oxidation ($NO + O_2$)	NO, 1500; $15000 < O_2 < 80000$	150–450	0.36