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Catalytic decomposition of nitrous oxide on “in situ” generated thermally calcined hydrotalcites

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Abstract

Catalytic decomposition of nitrous oxide to nitrogen and oxygen has been carried out on “in situ” generated thermally calcined hydrotalcites of the general formula $M\text{-Al-CO}_3\text{-HT}$, where M stand for Ni, Co and Cu, in the temperature range 140–310°C at 50 Torr (1 Torr = 133.3 Pa) initial pressure of the gas. All the catalysts showed first-order dependence on nitrous oxide without any inhibition by oxygen. Among the catalysts studied, Ni-Al-CO₃-HT was the most active, followed by the cobalt and copper catalysts. These catalysts are more active in comparison with earlier reported Cu-ZSM-5, Co-ZSM-5 and Rh-ZSM-5 catalysts based on their conversion for the decomposition. The enhanced activity can be attributed to non-stoichiometry and dispersion of the active mixed metal oxides. Prior to the kinetic runs, the catalytic precursors were characterised by X-ray diffraction, thermogravimetry-differential scanning calorimetry measurements, IR, transmission electron microscopy and nitrogen adsorption measurements.

Key words dispersion, hydrotalcites, mixed metal oxides, nitrous oxide decomposition

INTRODUCTION

Nitrous oxide, an environmental pollutant, is responsible for the depletion of the ozone layer and for the greenhouse effect [1,2]. The concentration of this gas increases in the atmosphere due to industrial and anthropogenic activities. To protect the environment the nitrous oxide formed must be decomposed. Decomposition of nitrous oxide to nitrogen and oxygen has been carried out on a wide variety of catalysts, such as metal oxides, mixed metal oxides and metal exchanged zeolites [3–7]. Most of the previous reports were concerned with the kinetics of the decomposition rather than with the conversion levels. Recently, Li and Armor [8] carried out a catalytic decomposition of nitrous oxide on metal-exchanged zeolites and showed that Cu-ZSM-5 and Rh-ZSM-5 are the best catalysts to date.

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Hydrotalcite-like materials are layered mixed metal hydroxides [9–11] possessing a brucite network in which the divalent ion is substituted by a trivalent ion whose excess positive charge is compensated for by anions occupying the interlayer positions. Thermal calcination of these materials results in the formation of interactive non-stoichiometric, well dispersed mixed metal oxides which are extensively used in many catalytic transformations such as steam reforming, carbon monoxide methanation and higher alcohol synthesis [12–14]. The above mentioned properties of the finished catalysts can be utilised for the catalytic decomposition of nitrous oxide on thermally calcined hydrotalcite-like materials. In this communication, we report the activities of catalysts derived from thermal treatment of hydrotalcites of the general formula $M\text{-Al-CO}_3\text{-HT}$ where M stands for Ni, Co and Cu, and compare their activities with the catalysts previously reported in the literature.

EXPERIMENTAL

The hydrotalcite-like materials (HT-like) were prepared by the method employed by Reichle [15] wherein sequential precipitation of metal nitrates was carried out using a NaOH and Na_2CO_3 mixture. The precipitate obtained was aged at 65°C for 24 h. It was then filtered, washed with distilled water and dried at 70°C overnight. Elemental analysis for M^{2+} and M^{3+} was carried out by inductively coupled plasma emission spectroscopy (ICPES) (Model 3410, ARL) by dissolving the compounds in a minimal amount of hydrochloric acid. X-ray diffraction of the samples was performed in a Philips X-ray generator (Model PW1130) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) except for the Co-containing compound, for which $\text{Co K}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$) was used. Thermogravimetric analysis (TGA) spectra of these compounds were recorded in a Perkin-Elmer TGA7 in the temperature range $50\text{--}900^\circ\text{C}$ at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The surface areas of the samples were measured according to the BET adsorption method using a Carlo-Erba (Model 1800) sorptometer at 77 K.

Kinetic measurements were carried out in an all-glass recirculatory static reactor (130 cm^3). About 1 g of the precursor — hydrotalcite — was used for the catalytic studies. Thermal calcination of the material was done in vacuum to generate “in situ” mixed metal oxide active catalysts. The decomposition of nitrous oxide was carried out at 50 Torr (1 Torr = 133.3 Pa) initial pressure of the gas in the temperature range $140\text{--}310^\circ\text{C}$. Before each kinetic run, the catalyst was evacuated to 10^{-5} Torr at the activation temperature (300°C for Ni-Al- $\text{CO}_3\text{-HT}$, 350°C for Co-Al- $\text{CO}_3\text{-HT}$ and 400°C for Cu-Al- $\text{CO}_3\text{-HT}$) for 5 h and soaked in oxygen for 12 h at the reaction temperature. The reaction was then carried out after evacuating the gas phase and the physisorbed oxygen for 2 min. The reproducibility of each run was confirmed experimentally, indicat-

ing the regeneration of the active surface upon employing the above pretreatments.

RESULTS AND DISCUSSION

Table 1 summarises the physico-chemical properties of these HT-like materials. The X-ray diffraction patterns of these materials, given in Fig 1, resemble the pattern of natural mineral hydrotalcite (except Cu-Al-CO₃-HT which showed also a malachite pattern) exhibiting sharp and symmetric peaks for the (003), (006), (110) and (113) planes and broad and asymmetric peaks for the (102), (105) and (108) planes characteristic of clay minerals having a layered structure [16]. Thermogravimetric analysis on these materials showed two stages of weight loss, the first one occurring in the temperature range 200–250 °C, attributed to the removal of weakly bound and interlayer water molecules, while the second peak at 300–350 °C accounted for the removal of water from the brucite network and carbon dioxide from the interlayer anion, resulting in the destruction of the layered structure. In the case of Cu-Al-CO₃-HT, loss of interlayer water, structural water and carbon dioxide occur simultaneously in the temperature range 100–250 °C. In the case of Co-Al-CO₃-HT during evacuation in vacuum at 2.67 Pa at 120 °C, a colour change from pink to black was observed and the resulting compound showed a diffraction pattern of a spinel-like structure [17]

TABLE 1

Physico-chemical properties of M-Al-CO₃-HT where M=Co, Ni and Cu

Properties	Ni-Al-CO ₃ -HT	Co-Al-CO ₃ -HT	Cu-Al-CO ₃ -HT
Colour	Green	Pink	Blue
Chemical analysis M(II)/M(III) (atomic ratio)	3.0	3.0	2.9
XRD			
a Phase obtained	HT ^a	HT	HT + malachite
b Lattice parameters	$a=3.030 \text{ \AA}$ $c=22.740 \text{ \AA}$	$a=3.095 \text{ \AA}$ $c=22.751 \text{ \AA}$	$a=3.070 \text{ \AA}$ $c=20.170 \text{ \AA}$
TGA			
a Net weight loss (%)	32.6	29.7	37.7
b Transition temperatures T_1, T_2 (K)	485, 615	444, 518	383, 524
Surface area (m ² /g)	114	72	35

^a Hydrotalcite

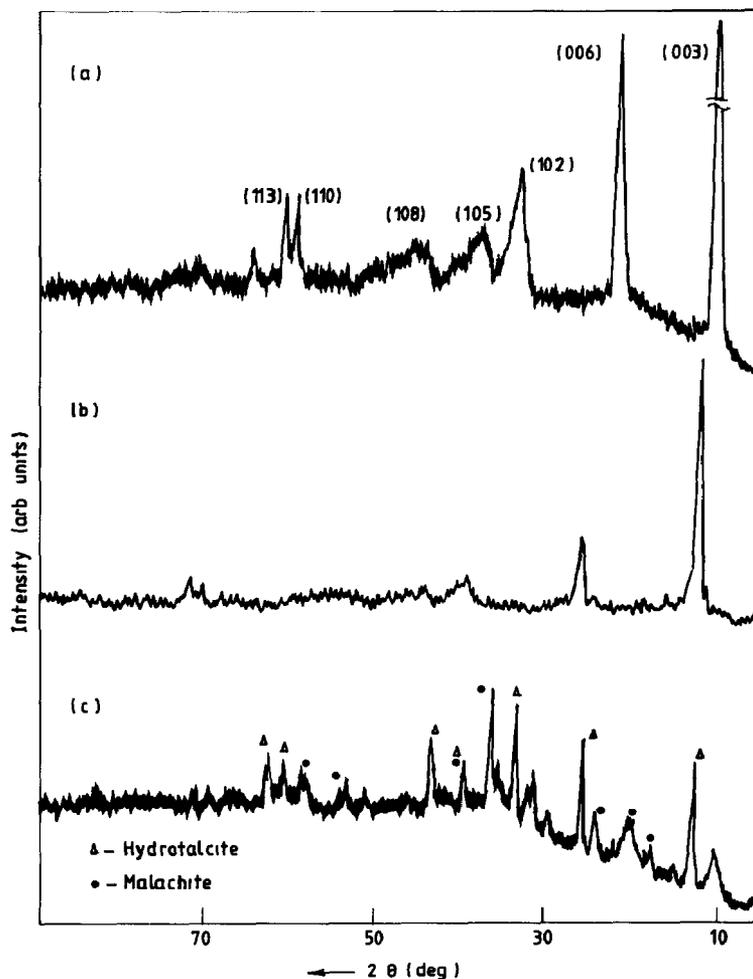


Fig 1 XRD patterns of freshly prepared samples (a) Ni-Al-CO₃-HT, (b) Co-Al-CO₃-HT, (c) Cu-Al-CO₃-HT

Thermal calcination of these materials resulted in the formation of mixed metal oxides. The X-ray diffraction pattern of Ni-Al-CO₃-HT showed that up to 200°C the HT-like network is preserved. Further increase in the temperature leads to the destruction of the layered network, resulting in the formation of NiO as evidenced from X-ray diffraction (XRD). The crystallinity of the NiO obtained increases with increase in the calcination temperature. It has been reported that at very high temperatures spinel formation of NiAl₂O₄ is

observed [18]. In the case of Co-Al-CO₃-HT, spinel formation occurs at 200°C and the crystallinity of the spinel increases with increase in calcination temperature. In the case of Ni-Al-CO₃-HT, the surface area increases up to 300°C and then starts to decrease. The decrease in the surface area is less, which is attributed to the strong interaction between NiO and Al₂O₃, forming a solid solution and thereby preventing the sintering of the NiO particles (Fig 2) [13]. However, in the case of Co-Al-CO₃-HT the decrease in the surface area with increase in temperature is attributed to sintering of the particles. These data also substantiate the increase in the crystallinity of mixed metal oxides upon increase in calcination temperature.

The kinetic data (see Table 2) for the decomposition of nitrous oxide on the "in situ" calcined hydrotalcites have been evaluated using eqn (1), corresponding to the situation of no inhibition by product oxygen

$$-dP_{\text{N}_2\text{O}}/dt = k_1 P_{\text{N}_2\text{O}} \quad (1)$$

where $P_{\text{N}_2\text{O}}$ is the initial pressure of the nitrous oxide. Comparison of the activities were made on the basis of rate constants for the decomposition of nitrous oxide, which decreases in the following order: Ni-Al-CO₃-HT > Co-Al-CO₃-HT > Cu-Al-CO₃-HT. For the evaluation of the kinetic data the conversions were restricted to less than 20%

Fig. 3 shows a plot of the conversion against temperature of these catalysts for the decomposition of nitrous oxide, along with Cu-ZSM-5, Co-ZSM-5 and Rh-ZSM-5 [8]. Cu-ZSM-5 and Co-ZSM-5 showed appreciable conversion only

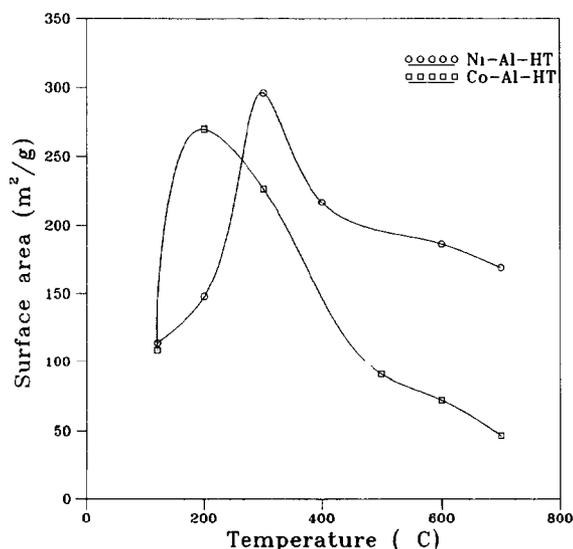


Fig 2 Variation of surface area with calcination temperature for Ni-Al-CO₃-HT and Co-Al-CO₃-HT

TABLE 2

Kinetic parameters for the decomposition of nitrous oxide at 50 Torr on M-Al-CO₃-HT

Compound	Temp (C)	$k (\times 10^{-3})^a$	E_a (kJ/mol)	lnA	Conversion at 30-min time interval (%)
Ni-Al-CO ₃ -HT	140	2 058	54.7	9.73	6.0
	160	4 000			11.1
	170	5 950			16.9
	180	8 333			21.3
Co-Al-CO ₃ -HT	160	3 652	46.8	7.40	10.4
	170	5 000			13.8
	180	6 473			17.0
	190	7 878			21.0
Cu-Al-CO ₃ -HT	280	2 702	53.9	5.82	7.7
	290	3 250			9.3
	300	4 137			10.4
	310	5 000			14.0

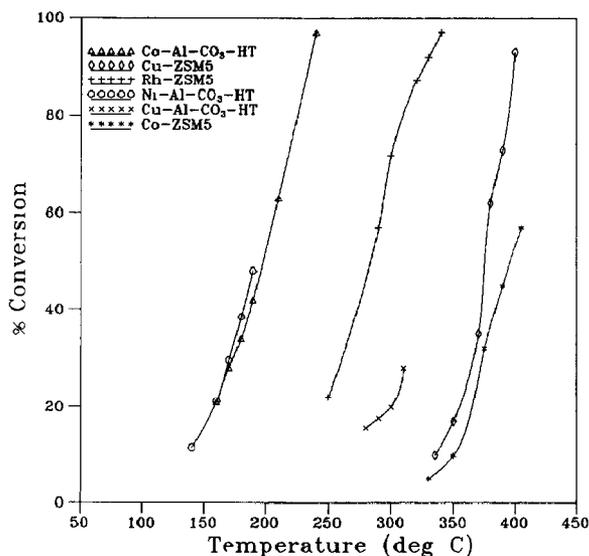
^a Unit of k for no inhibition by oxygen min^{-1} 

Fig 3 Nitrous oxide conversion on various catalysts as a function of temperature

at 330°C and reached 100% and 50% conversion at 400°C, respectively. Rh-ZSM-5 and Ru-ZSM-5 showed appreciable conversion at 250°C and reached their 100% conversion at 350°C. In the case of our catalysts, Ni-Al-CO₃-HT

and Co-Al-CO₃-HT showed appreciable activity even at 150°C whereas the Cu-containing catalyst showed appreciable activity around 300°C. Ni-Al-CO₃-HT and Co-Al-CO₃-HT reached their 50% and 100% conversion levels at 190°C and 250°C, respectively, which is 100°C less than the most active catalyst reported in the literature so far [8]

Analysis of the spent catalysts were done using X-ray diffraction (Fig. 4) in an attempt to explain the high activity of these catalysts. In the case of spent Ni-Al-CO₃-HT, only NiO is observed whose d_{110} is 2.045 Å, which is lower than the ASTM value (2.088 Å) suggesting that some of the Al³⁺ ions dissolved in NiO forming a solid solution represented by NiAl_{2x}O_{1+3x}. Co-Al-CO₃-HT spent catalyst showed a diffraction pattern of a spinel phase whose d_{311} is 2.421 Å, which is less than the d_{311} of pure CoAl₂O₄ (2.443 Å) and Co₃O₄ (2.438 Å) indicating it to be non-stoichiometric. In the case of spent Cu-Al-CO₃-HT,

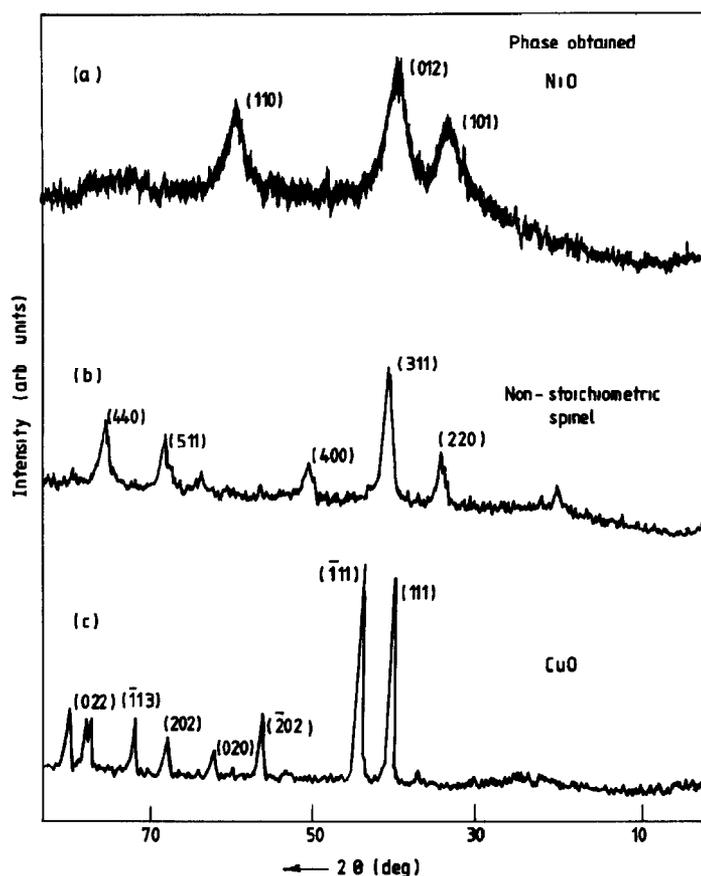


Fig 4 XRD patterns of spent catalysts (a) Ni-Al-CO₃-HT, (b) Co-Al-CO₃-HT, (c) Cu-Al-CO₃-HT

highly crystalline CuO was observed, which was supposed to result from a malachite phase dispersed in the alumina matrix [12]. The surface area of these materials under the reaction conditions lies in the range 200–300 m²/g. The fact that the active metal oxides are dispersed in a high surface area matrix, together with the non-stoichiometry of the metal oxides could be the reason for the high activities observed for the decomposition of nitrous oxide

CONCLUSIONS

Catalytic decomposition of nitrous oxide was carried out on different HT-like compounds, their order of activity being Ni > Co > Cu. We have reported that nickel and cobalt containing catalysts showed substantial activity even at 150°C for this reaction. They showed 50% and 100% conversion at 190°C and 250°C, respectively, which is 100°C less than the most active catalyst reported in the literature. A detailed physico-chemical characterization of the precursors has also been carried out from which the activation conditions for this reaction were derived. Cu-containing hydrotalcite, although low in activity among the catalysts studied, is also very active in comparison with the other active catalyst, Cu-ZSM-5. Therefore, these hydrotalcite-like materials possess unique features, which, upon thermal calcination, lead to the formation of active sites which are responsible for the very high activity.

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