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Calcined hydrotalcites for the catalytic decomposition of N_2O in simulated process streams

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Abstract

Various hydrotalcite based catalysts were prepared for testing for the catalytic decomposition of N_2O. Co–Al, Ni–Al, Co/Pd–Al, Co/Rh–Al, and Co/Mg–Al substituted hydrotalcites and Co–La–Al hydroxides offer very good activity at modest temperatures. Precalcination of these materials at ca. 450–500°C, which destroys the hydrotalcite phase, is necessary for optimum activity and life. For Co substituted hydrotalcites, the optimal ratio of Co/Al is 3.0. The temperature for 50% conversion of N_2O of these calcined cobalt hydrotalcites is ca. 75°C lower than for the previous highly active Co-ZSM-5. These calcined cobalt hydrotalcite materials display sustained life at temperatures in excess of 670°C in an O_2 rich, wet stream with high levels of N_2O [10%]. Excess O_2 does not seriously impact N_2O decomposition, but the combination of both water vapor and O_2 does reduce activity by ca. 50%.

Keywords: N_2O; Decomposition; Hydrotalcite; Co-ZSM-5; Life; Water vapor effect; Calcination

1. Introduction

Nitrous oxide (N_2O) is an environmental pollutant because it contributes to catalytic destruction of stratospheric ozone and is a greenhouse gas. N_2O continues to increase in the atmosphere, and this increase appears to be caused mainly by anthropogenic activities [1–4]. Man-made N_2O may arise as a co-product from some chemical processes, such as the use of circulating fluidized beds for combustion [5–7] and the production of large amounts of adipic acid for Nylon 6,6 [1,8].

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In addition small amounts of N_2O are emitted from millions of automobiles [9–11].

Several metal oxides [12–14] and mixed metal oxides, principally perovskites [15–17] show some activity for N_2O decomposition, but the reaction rates were too low [18] to have any industrial significance [19]. Porta and coworkers [20] studied the structure and catalytic activity of $Co_xMg_{1-x}Al_2O_4$ spinel solid solutions for use as catalysts in decomposing N_2O into gaseous nitrogen and oxygen. Here, the catalytic activity per cobalt ion in various N_2O decomposition catalysts was found to increase with increasing dilution with MgO. The distribution of cobalt ions between octahedral and tetrahedral sites in the spinel structure of $Co_xMg_{1-x}Al_2O_4$ was found to vary with temperature, and the fraction of cobalt ions in octahedral sites was found to increase with increasing quenching temperature. They concluded that catalyst activity generally increases as a greater amount of cobalt ions is incorporated into octahedral sites in the structure.

More recently, there have been reports of several metal zeolites as catalysts for N_2O decomposition [21,22]. In 1992, it was reported [19,23] that selected metal exchanged zeolites, principally Cu, Co, Rh or Pd-ZSM-5, were very active for N_2O decomposition. However, the sensitivity of Cu-ZSM-5 to water vapor at high temperatures makes it unattractive [24] as a commercial catalyst. Indeed, further studies in this area indicated that these catalysts should be tested under wet atmospheres [24,25] for this exothermic reaction in order to truly simulate process conditions (typically ca. 10% N_2O, ca. 1% water vapor, in air).

Earlier, Reichle [26] and Reichle and coworkers [27] reported that various anionic clay minerals belonging to the pyroaurite-sjogrenite group, such as hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3^{2-}) \cdot 4H_2O$ can thermally decompose to form a product that is a useful catalyst for vapor-phase aldol condensations. Replacement of Mg by Fe, Co, Ni and Zn and/or replacement of Al by Fe and Cr also results in isomorphous double hydroxides which, on heat treatment, are rendered catalytically active. The activity of the catalyst is strongly affected by the temperature at which the hydrotalcite is activated. Recently, Kannan and Swamy reported that calcined Co, Cu or Ni hydrotalcites [HT] were effective catalysts [28] for N_2O decomposition. These catalysts were tested in a recirculating, static reactor with 50 torr of N_2O; these experimental conditions do not resemble true process conditions. We have now extended and optimized the materials identified earlier by Kannan and Swamy. This manuscript describes optimal calcined, cobalt hydrotalcite [HT] catalysts for N_2O decomposition and compares their performance to Co-ZSM-5 under simulated process conditions [29].

2. Experimental

2.1. Preparation of hydrotalcite catalysts

Details for preparation of the various hydrotalcite derived catalysts are given below. Before activation these clays were dried at 100°C in air overnight and then

activated at temperatures up to 500°C. Calcination at high temperatures produces a mixed metal oxide catalyst with poor crystallinity as evidenced from X-ray diffraction. The heat treatment temperature used to convert the anionic clay material to the active catalyst can be varied widely but at temperatures less than about 200°C, the desired mixed metal oxides are formed slowly and incompletely.

Inductively coupled plasma emission spectroscopy was used to analyze for the metal ions and Na^+. X-ray diffraction patterns of the samples were taken using a Philips X-ray generator (Model PW1130) using Cu Kα radiation ($\lambda = 1.5418$ Å) except for Co-containing compound wherein Co Kα radiation ($\lambda = 1.7902$ Å) was used. Surface areas were measured by the standard BET technique using N_2.

2.2. Cobalt–aluminum hydrotalcite having a Co/Al molar ratio of 2.0

A solution of 58.21 g (0.20 mol) cobalt nitrate hexahydrate and 37.5 g (0.10 mol) of aluminum nitrate nonahydrate in 70 cc of distilled water was added dropwise (over a 4 h period at room temperature) to a solution containing 28.87 g (0.70 mol) 97% NaOH, 20.03 g (0.189 mol) sodium carbonate and 2.2 mol distilled water. The precipitate was stirred for 30 min, heated to 65°C for 16 h, filtered, washed with large amounts of distilled water to remove excess sodium and nitrate, and dried at 100°C. (Analyses: 54.7% Co by weight, 11.2% Al by weight, Co/Al(atom) = 2.23, $d(003) = 7.58$ Å.) XRD and IR confirmed that the compound prepared is single phase in nature with hydrotalcite-like structure. XRD showed sharp and symmetric reflections for (003), (006) and (110) planes indicating the pattern structure characteristic of clay minerals possessing a layered structure. TGA studies showed two stages of weight loss. The first weight loss occurred between 150 and 200°C and the second occurred between 225 and 275°C. This result was substantiated by differential scanning calorimetry results which showed two endothermic peaks corresponding to the two weight losses.

2.3. Nickel–aluminum hydrotalcite having a Ni/Al molar ratio of 2.0

A solution of 58.16 g nickel nitrate hexahydrate and 34.51 g of aluminum nitrate nonahydrate in 140 cc of distilled water was added dropwise (over a 4 h period at room temperature) to 228 cc solution of 28.87 g 97% NaOH and 20.03 g sodium carbonate while maintaining the temperature at or below room temperature. The precipitate was stirred for 30 min, heated to 65°C for 16 h, filtered, washed with large amounts of distilled water to remove excess sodium and nitrate, and dried at 110°C. (Analyses: 56.1% Ni by weight, 13.1% Al by weight, Ni/Al(atom) = 1.97; $d(003) = 7.55$ Å.)

2.4. Copper-aluminum hydrotalcite having a Cu/Al molar ratio of 2.0

A solution of 23.26 g cupric nitrate pentahydrate and 18.76 g of aluminum nitrate nonahydrate in 140 cc of distilled water was added dropwise (over a 3 h period at

room temperature) to 114 cc solution of 14.44 g 97% NaOH and 10.02 g sodium carbonate while maintaining the temperature at or below room temperature. The precipitate was stirred for 60 min, heated at 65°C for 18 h, filtered, washed with large amounts of distilled water to remove excess sodium and nitrate, and dried at 110°C. (Analyses: 66.0% Cu by weight, 12.6% Al by weight, Cu/Al = 2.22.)

2.5. Cobalt, magnesium–aluminum hydrotalcite [Co/Mg/Al ratio of 2/1/1]

A solution containing Co^{2+}, Mg^{2+} and Al^{3+} was made by dissolving 29.1 g $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mol), 12.8 g $Mg(NO_3)_2 \cdot 6H_2O$ (0.05 mol) and 18.8 g ($Al(NO_3)_3 \cdot 9H_2O$ (0.05 mol) in 75 ml of deionized water at room temperature. A second solution was made by dissolving 14 g NaOH (0.35 mol) and 10.6 g Na_2CO_3 (0.1 mol) in 100 ml of deionized water at room temperature. The second solution was slowly added (drop-by-drop) to the first solution at room temperature over a period of 1 h with vigorous stirring. The final pH of the suspension was 10. The precipitates were aged at 65°C for 18 h with good mixing. The resulting product was then filtered, washed with 300 ml of water in a beaker and filtered again. Finally, the material was dried in an oven at 110°C in air overnight. The yield was 18.0 g. Elemental analyses of this sample show Co/Al = 1.97 and Mg/Al = 0.94. The $d(003)$ spacings were found to be 7.69 Å by X-ray diffraction.

2.6. Cobalt–rhodium, aluminum hydrotalcite [Co/Rh/Al molar ratio of 1/0.2/1]

A solution of 1.0 g (10% Rh) rhodium nitrate, 28.81 g cobalt nitrate hexahydrate and 18.76 g of aluminum nitrate nonahydrate in 114 cc of distilled water was added dropwise (over a 0.5 h period at room temperature) to a 114 cc solution of 14.44 g 97% NaOH and 10.02 g sodium carbonate while maintaining the temperature at or below room temperature. The precipitate was stirred for 2 h, heated to 65°C for 18 h, filtered, washed with large amounts of distilled water to remove excess sodium and nitrate, and dried at 110°C. The anionic clay material prepared according to this method corresponds to the replacement of a portion of the aluminum by rhodium. (Analyses: 58.3% Co by weight, 11.9% Al by weight, Co/Al = 2.24, Rh/Al = 0.016; $d(003)$ = 7.54 Å.)

2.7. Preparation of Co-ZSM-5

The preparation of Co-ZSM-5 by repetitive exchange of aqueous cobalt acetate solutions with NH_4-ZSM-5 at 80°C was described earlier (Co/Al = 0.53) [25,26]. ZSM-5 (Si/Al = 11) was purchased from VAW AG [Schwandorf, Germany].

2.8. Catalytic testing for N_2O decomposition

For screening catalyst activity as described in Table 1 and Table 2, experiments were carried out at an ambient pressure with 0.1 g of catalyst in a quartz reactor

Table 1
Effect of Co/Al ratio on N_2O decomposition using a cobalt–aluminum hydrotalcite catalyst calcined at 500°C[a]

Catalyst Co/Al Ratio	BET area (m^2/g)	N_2O conversion (%) 300°C	350°C	400°C	450°C	500°C
1.1	164	8	12	22	45	79
2.0		9	17	36	68	93
2.55		16	27	49	81 (61[b], 17[c])	N/A
3.0	100	13	24	53	84 (67[b], 25[c])	N/A
3.55		10	18	49	82 (61[b], 14[c])	N/A

[a] Test conditions: 985 ppm N_2O in He; 0.1 g sample; total flow = 100 cm^3/min.
[b] With 2.5% oxygen.
[c] With 2% water and 2.5% oxygen.

tube. To reduce pressure drop, the catalyst was pelletized, crushed and then sieved to 60–80 mesh before use. The reactor was heated by a temperature-controlled furnace and the temperature was monitored by a K-type thermocouple in contact with the catalyst bed. The total flow rate of the feed was 100 cm^3(STP)/min (GHSV = 30 000) using Brooks 5850 mass flow meter/controllers. The concentration of N_2O was 985 ppm balanced by He. Oxygen (2.5%) was added for some runs. H_2O (2%) was added to the feed via a H_2O saturator, and the level of H_2O added was controlled by adjusting the temperature of this saturator. The activity measurements were made using this microcatalytic reactor in a steady-state flow mode. Product analysis was obtained using an on-line gas chromatograph with a

Table 2
Catalyst activity for various compositions in N_2O decomposition[a]

Catalyst[d]	Catalyst composition	BET area m^2/g	N_2O conversion (%) 300°C	350°C	400°C	450°C	500°C
Cu–Al–HT	Cu/Al = 2.0	N/A	10	12	24	48	81
Ni–Al–HT	Ni/Al = 3.0	149	12	25	66	95 (92[b], 9[c])	N/A
Co-ZSM-5	Co/Al = 0.53	N/A	8	18	59	92 (92[b], 25[c])	N/A
Co, Pd–Al–HT	Co/Al = 2.19 Pd/Al = 0.045	102	11	27	59	90	N/A
Co–Al–HT	Co/Al = 3.0	100	13	24	53	84 (67[b], 25[c])	N/A
Co, Mg–Al–HT	Co/Mg/Al = 2/.94/1	93	36	66	94	100 (99[b], 88[c])	N/A
Mg–Al–HT	Mg/Al = 2.2	N/A	1	1	1	1	2
Co–Rh, Al–HT	0.3 wt % Rh	N/A	56	72	98	100 (99[b], 88[c])	N/A
Co–Rh, Al–HT	0.7 wt. % Rh	119	100 (7[c])	N/A	100 (67[c])	100 (100[b], 100[c])	N/A
Co–Ru, Al–HT	1.0 wt% Rh	N/A	9	16	38	71 (42[b], 12[c])	N/A
Co–La, Al–HT	Co/La/Al = 4/1/1	N/A	79	92	98	100	100
Co–Zn–Al–HT	Co/Zn/Al = 1.5/1.5/1	N/A	13	27	44	70	921

[a] Test conditions: 985 ppm N_2O in He; 0.1 g sample; flow rate = 100 cm^3/min.
[b] With 2.5% oxygen
[c] With 2% water and 2.5% oxygen
[d] All calcined to 500°C, except for Cu–Al–HT at 550°C
N/A = not available.

thermal conductivity detector. The separation column was packed with Porapak Q (80/100 mesh) and was 4 ft. long having a 1/8 in. outer diameter. The oven temperature of the chromatograph was 25°C and the flow rate of the carrier gas was 30 cm^3/min. Once we were convinced of product composition, N_2O conversion was monitored via the production of N_2 using a molecular sieve 5A column (1/8 in. × 10 ft.) at 25°C.

For simulated process runs a larger flow reactor was used. For adding water vapor, an ISCO pump was used to inject water into the gas stream. The injection port was located in the reactor preheated zone to allow for rapid vaporization and provide sufficient mixing time. A Servomex Model 1175 O_2 analyzer was used to measure O_2; a Thermo-Environmental Model 10 chemiluminescence analyzer was used to measure NO and NO_x. Four separate runs were conducted in the large flow reactor using 15–25 g Co-ZSM-5 or cobalt–HT catalyst. The Co-ZSM-5 catalyst was an extrudate, either in the form of 1/10 in. trilobes or 1/8 in. extrudates (prepared using an alumina binder [24]). Prior to testing, the Co-HT catalysts were calcined at 500°C and then pressed to form 10–16 mesh particles. The reactor was fabricated from 1 in. schedule 40 steel pipe. To study catalyst life, the amount of catalyst and the concentration of N_2O in the feed were adjusted to represent simulated process conditions. The reaction temperatures ranged from 200 to about 800°C.

3. Results and discussion

The results presented in Table 1 compare reaction conversions of N_2O to N_2 and O_2 obtained using calcined cobalt–aluminum hydrotalcite catalysts having varied ratios of cobalt and aluminum cations as a function of temperature. The Co/Al ratio was varied from 1.1 to 3.55 for decomposing N_2O in a helium stream containing 985 ppm N_2O and alternately, 2.5% oxygen or 2.5% oxygen and 2% water vapor. The results demonstrate that N_2O conversion for each of the runs increases with increasing reaction temperature with the best results obtained at Co/Al = 3.0 which exhibits 84% N_2O conversion at a reaction temperature of 450°C. The presence of oxygen or oxygen and water vapor in the N_2O containing gaseous mixture does reduce N_2O conversion.

Independent tests revealed that N_2O conversion is maximized when the catalyst is calcined at a temperature ranging from 400 to 500°C; calcination at 800°C is too severe. While O_2 has a slight effect upon N_2O conversion, the addition of both O_2 and H_2O have a significant impact on conversion at 450°C.

The results presented in Table 2 compare the conversions of N_2O to gaseous nitrogen and oxygen obtained using calcined anionic clay materials containing copper, nickel, rhodium, cobalt or palladium versus conversion over Co-ZSM-5. These catalysts were pre-calcined ex-situ at 500°C for 4 h in air. Calcined Ni-Al-hydrotalcite provides comparable N_2O conversion to Co–Al HT at a process tem-

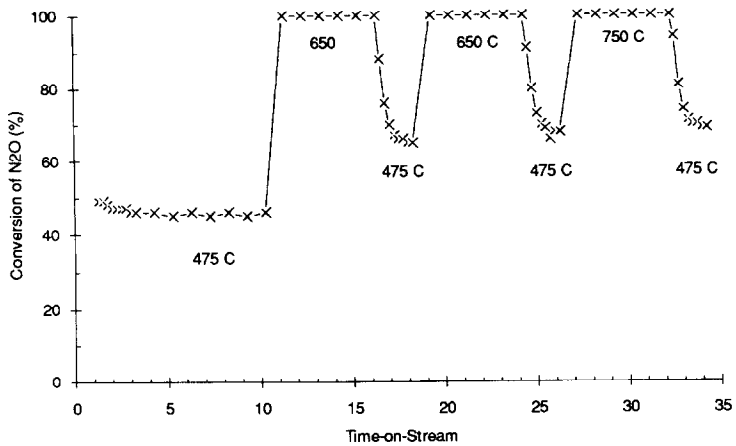

Fig. 1. Activity of Co–HT catalyst (Co/Al = 2.2) with time [15% N_2O, 2% H_2O and the balance helium over a 30 h period; 0.25 g of the catalyst was utilized at a GHSV of 18 000]; from Ref. [29].

perature of 450°C in the absence or presence of oxygen and water. The calcined Co–Mg, Al hydrotalcite catalyst also shows improved activity at low temperatures compared to Co–Al HT. When Al^{3+} is partially replaced by La^{3+} (Al/La = 1), the resulting Co–Al La–HT material did not reveal any hydrotalcite structure by XRD analysis, but after standard thermal activation it also gave high activity at low temperature (79% at 300°C). The results demonstrate excellent conversion of N_2O to N_2 and O_2 is achieved with a calcined cobalt–rhodium aluminum hydrotalcite which, provides 100% conversion of N_2O to gaseous nitrogen and oxygen at a process temperature of 300°C. This is ca. 150°C lower than the 450°C temperature required for Co-ZSM-5 to yield comparable conversion.

Fig. 1 illustrates conversion of N_2O to gaseous nitrogen and oxygen obtained as a function of time and temperature using a cobalt–aluminum hydrotalcite catalyst which was calcined at 500°C. This shows that N_2O decomposition activity of this catalyst is not markedly affected by exposure to a simulated water-containing N_2O

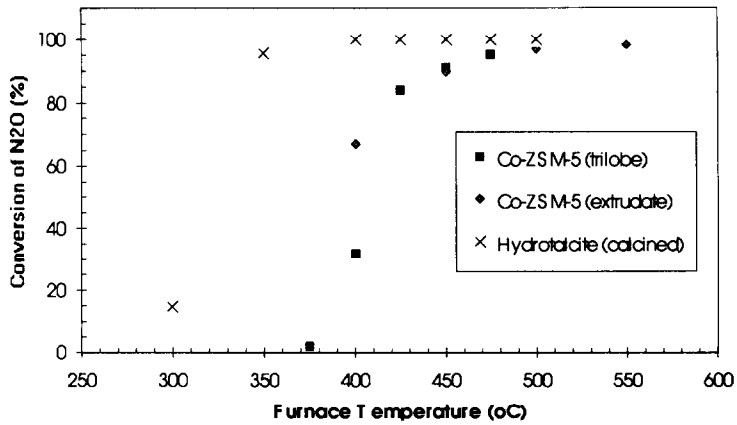

Fig. 2. Activity of Co–AlHT (Co/Al = 2.2) versus Co-ZSM-5 as a function of catalyst inlet. Catalyst activity for N_2O decomposition using various cobalt-containing catalysts.

process stream (15% N_2O, 2% H_2O and the balance helium) over a 30 h period (0.25 g of the catalyst was utilized at a GHSV of 18 000). The two inlet temperatures in Fig. 1, 650 and 750°C, were chosen to stress the catalyst under extreme conditions in order to accelerate any hydrothermally induced deactivation. These are temperature extremes to be expected under commercial reaction conditions. The catalyst activity was then monitored at 475°C, wherein there was an increase in performance by 20 percentage points after the initial exposure to 650°C. Once treated under this set of conditions, the activity did not change further upon cycling between 475 and 750°C. Fig. 1 also illustrates that conversion of N_2O to gaseous nitrogen and oxygen approaches 100% at a process temperature of 650°C and ca. 65% at a process temperature of 475°C. The desired conversion level can be achieved by adjusting the process operating temperature or space velocity.

Using a cobalt–aluminum hydrotalcite catalyst that was calcined in air at 500°C in a process stream containing 10% N_2O, 2% H_2O, 2% O_2 and the balance N_2, GHSV = 18 500 at 1.7 bar (a slight back pressure was maintained on the catalyst bed), the temperature of the catalyst bed increased to about 670°C due to the exothermic nature of the N_2O decomposition reaction [inlet temperature = 500°C]. The conversion of N_2O to N_2 and O_2 approaches 100% at a process temperature of 670°C. It is important to realize that with a large bed of catalyst, one can observe a substantial increase in bed temperature, due to this very exothermic reaction. The activity of the catalyst was not markedly affected by oxygen or moisture in the N_2O containing gaseous mixture over the 175 h test period [29].

Fig. 2 illustrates conversion of N_2O to gaseous nitrogen and oxygen obtained as function of catalyst inlet temperature using a Co–Al–HT catalyst versus Co-ZSM-5 in either trilobed or extrudate form [25]. Experiments were conducted using a feed stream containing 10% N_2O, 2% water, 2% oxygen and the balance nitrogen. Reactor pressure was maintained at 10 psig and GHSV was maintained between 16 000 and 18 000. While both the hydrotalcite catalyst and Co-ZSM-5 catalyst provide high conversion of N_2O to N_2 and O_2, the calcined hydrotalcite catalyst demonstrates a light off temperature at least 75°C lower than Co-ZSM-5. The lower light off temperature (temperature corresponding to 50% conversion of N_2O) for the Co–Al–HT catalyst represents a significant process advantage since energy requirements are reduced and less wear and stress are placed upon process equipment.

The surface area of the catalysts is substantially affected by heat treatment temperature employed during preparation of such catalysts. The data demonstrate that the optimum heat treatment temperature for achieving maximum surface area varies depending upon catalyst composition. For example, maximum surface area for Ni–Al hydrotalcite is achieved using a heat treatment temperature of about 220°C while maximum surface area for Co–Al hydrotalcite is achieved using a heat treatment temperature of about 320°C.

4. Conclusion

Calcination of cobalt–aluminum hydrotalcites produces a relatively high surface area material that is quite effective for the catalytic decomposition of N_2O under simulated process conditions typical of emissions from facilities used for the production of Nylon 6,6. The calcined hydrotalcite catalysts offer enhanced activity over previous catalysts for removing N_2O from combustion processes. They are unexpectedly more active at lower process temperatures than previous catalysts in converting N_2O to N_2 and O_2. Large beds of these catalysts under simulated processing conditions were shown to perform effectively for > 175 h with a wet N_2O stream.

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