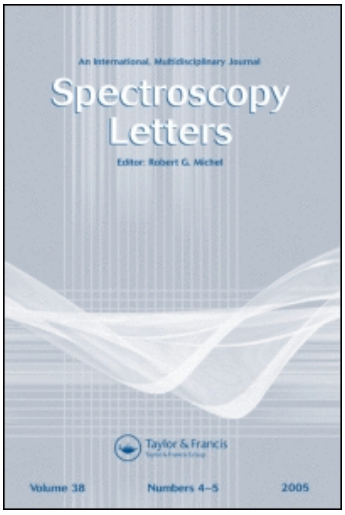

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IR CHARACTERISTICS AND CATALYTIC ACTIVITIES OF CU-CO-AL HYDROTALCITES

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IR CHARACTERISTICS AND CATALYTIC ACTIVITIES OF CU - CO - AL HYDROTALCITES

Key Words: Infrared Spectra; Hydrotalcite; Nitrous Oxide; Decomposition

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Abstract

Series of Co-Al and Co-Cu-Al hydrotalcites were synthesized, thermally activated and characterized. The correlation between the hydrotalcite composition and their IR spectra were discussed along with the results of X-ray diffraction analyses. The specific surface areas of hydrotalcites and their catalytic activities for nitrous oxide decomposition upon calcination were studied. As Co was partially replaced by Cu, the catalytic activity was improved by 10% under the same reaction conditions (Co/Cu/Al = 2.7/0.3/1). A spinel $Cu_xCo_{3-x}O_4$ was formed in calcined hydrotalcites.

1. Introduction

Hydrotalcites and related synthetic compounds are layered mixed metal basic carbonates of the general formula $[M_3Al(OH)_8]_2CO_3 \cdot 2H_2O$, where M=Mg, Ni, Fe, etc. These compounds possess positively charged brucite-like layers in which divalent ions are substituted by trivalent ions whose excess positive charges are compensated

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by exchangeable anions occupying the interlayer space along with water molecules. Thermal calcination of these materials results in the formation of interactive, well dispersed mixed metal oxides which are extensively used as catalysts for various purposes [1]. Recently, Kannan and Swamy [2] reported calcined Co, Cu and Ni hydrotalcites as effective catalysts for nitrous oxide decomposition. Later, Armor and his coworkers [3] optimized this catalytic reaction. The temperature for 50% conversion of nitrous oxide is about 75 K lower than the zeolite Co-ZSM-5. Nevertheless, mixed Cu-Co-Al oxides derived from hydrotalcites have never been tested for N_2O decomposition.

Bish and Brindley reported the infrared absorption spectra for takovite samples earlier [4]. The infrared spectra of hydrotalcite with M^{2+} / M^{3+} = 2/1 and M^{2+} / M^{3+} = 3/1 chemical ratios (where M^{2+}=Mg, Ni, or Fe, and M^{3+}=Al) were studied by Hernandez-Moreno and his coworkers [5]. Up to now, however, there is no report on the infrared spectra of series of Co-Al and Co-Cu-Al hydrotalcites, nor on the correlation between the IR spectra and the catalytic activity for nitrous oxide decomposition. In this communication, we present the IR characteristics of a series of Co-Al and Co-Cu-Al hydrotalcites, both uncalcined and calcined, and compare their catalytic activities for nitrous oxide decomposition.

2. Experimental

A series of Co-Al hydrotalcites and Cu-Co-Al hydrotalcites were prepared according to Reichle's method [1]. Cobalt and copper were precipitated together with aluminum from a mixed metal nitrate solution, when a NaOH and Na_2CO_3 mixture was added to the nitrate solution. The precipitate obtained was aged at 338 K for 16 h with stirring, and then filtered out, washed with large amounts of distilled water, dried at 373 K. Thermal calcination of the dried materials was conducted in air at 723 K for 5 hours.

The IR spectra of these compounds were recorded on a FTIR spectrometer (Model BIO-RAD FTS-20E) in the range of 4000-400 cm^{-1} using the KBr pellet technique. The formation of single-phase spinel or multiple phases was confirmed by recording X-ray diffractograms on a (D/Max-200Q) using Cu K_α radiation. The surface areas of the catalysts were obtained by the BET method, employing nitrogen adsorption at liquid nitrogen temperature.

The catalytic decomposition of nitrous oxide was tested in a fixed-bed flow-type apparatus. The reactor is a quartz tube with an inner diameter of 3 mm, filled with 0.10 ml catalyst. The catalyst was pelletized, crushed and then sieved to 60-80 mesh before use. Catalytic decomposition of nitrous oxide was carried out at 673 K and GHSV=15,000 h^{-1} with an initial N_2O concentration of 600 ppm. A gas chromatograph (SP-3410) with an ECD detector was used for measuring N_2O at the inlet and outlet of the catalytic reactor. A Porapak Q column (Φ4mm × 3m) was used for separation at 333 K.

3. Results and discussion

3.1. Infrared data combined with XRD analyses of uncalcined Co-Al hydrotalcite

Fig. 1 shows the IR spectra of a series of synthesized Co-Al hydrotalcites. The patterns agree with those of Mg- and Ni-substituted hydrotalcites given by Hernandez-Morenno [5]. The infrared bands can be classified into molecular vibrations of the constituent units, such as the hydroxyl groups and interlayer carbonate groups and lattice vibrations of the cation layers.

The broad band at around 3400-3600 cm^{-1}, which is present in all samples, can be attributed to the OH stretching vibration of the hydroxyl groups in these samples. The maximum of this band is shifted towards higher frequency with an increase of Co/Al ratio. This shift can be explained by the modification in the layer spacing upon metal substitution. Moreover, its broad appearance suggests the presence of hydrogen-bonded water molecules. The half-width of this band becomes narrower upon

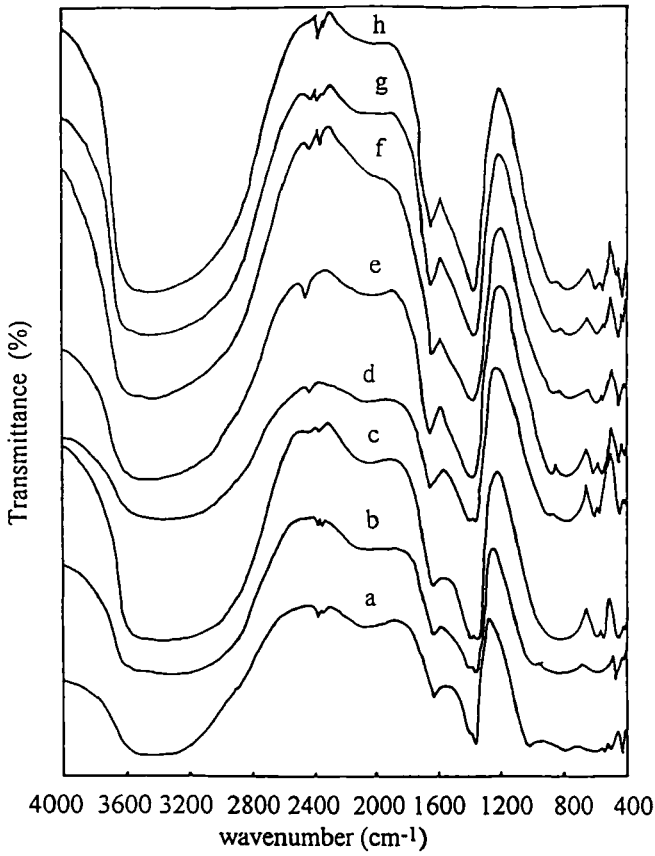

Fig. 1 IR spectra of uncalcined Co-Al hydrotalcites.
[a, b, c, d, e, f, g and h stand for Co/Al = 0.5, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 hydrotalcite respectively.]

calcination, as shown in Fig. 2. A H_2O bending vibration occurs at 1600cm^{-1}. A weak hydrogen bending band can be identified at around 1020 cm^{-1} for samples a and b, while in all the other samples with higher Co content the peak is shifted to 860 cm . Our argument is that samples a and b in Fig.1 contain a separate phase of $Al(OH)_3$ (Table 1), and this bayerite phase gives rise to this apparent peak at 1020 cm^{-1}.

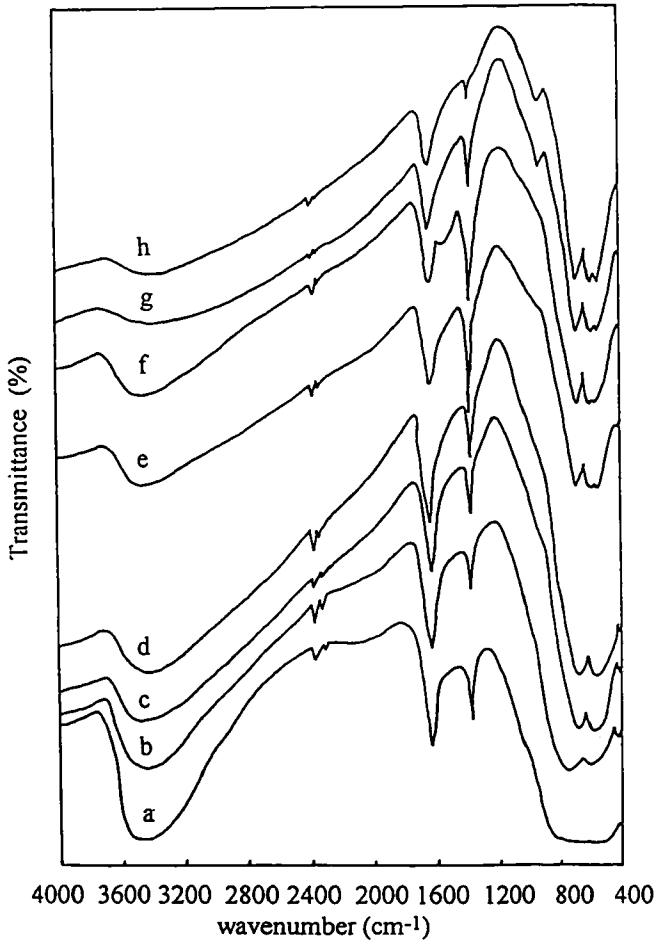

Fig. 2 IR spectra of calcined Co-Al hydrotalcites.
[a, b, c, d, e, f, g and h stand for Co/Al = 0.5, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 hydrotalcite respectively; Calcination temperature: 723K.]

Table 1

Co/Al ratio in hydrotalcites and their catalytic activities for N_2O decomposition* after calcination at 723K

Catalyst Co/Al ratio	Phases identified before calcination	Phases identified after calcination	BET area (m^2/g)	N_2O conversion(%)
0.5	hydrotalcite + $Al(OH)_3$	Co_2AlO_4	132.0	29.6
1.0	hydrotalcite + $Al(OH)_3$	Co_2AlO_4	166.9	35.0
2.0	hydrotalcite	Co_2AlO_4	128.3	33.2
2.5	hydrotalcite	$Co_2AlO_4 + Co_3O_4$	137.8	41.1
3.0	hydrotalcite	$Co_2AlO_4 + Co_3O_4$	143.2	84.9
3.5	hydrotalcite	$Co_2AlO_4 + Co_3O_4$	133.2	76.4
4.0	hydrotalcite	$Co_2AlO_4 + Co_3O_4$	115.7	70.2
5.0	hydrotalcite	$Co_2AlO_4 + Co_3O_4$	93.0	64.9

*Catalyst: 60-80 mesh; GHSV: 15000h^{-1}; Reaction temperature: 673K

Hernandez-Moreno et al. [5] also observed a stronger OH bending peak at 1005 cm^{-1} in case of $[Al_2Li(OH)_6]_2CO_3 \cdot nH_2O$ which contains no divalent metal ions.

In most hydrotalcites, the three vibration bands of carbonate anion are observed at 1350-1380 cm^{-1} (ν_3), 800 cm^{-1} (ν_2) and 610 cm^{-1} (ν_4). For the hydrotalcites with Co/Al ratio in the range of 3.0 ~ 5.0, only a single peak appears in the range of 1350-1380 cm^{-1}, that suggests the carbonate anion is in a symmetric environment characterized by a D_{3h} planar symmetry. However, in the range of Co/Al = 0.5 ~ 2.5 (curves a, b, c & d in Fig.1), a shoulder around 1400 cm^{-1} or a splitted band in the region 1350-1400 cm^{-1} appears, which can be attributed to a lowering of the symmetry of the carbonate (site of symmetry C_{2v}), and might also be attributed to the disordered nature of the interlayer [4, 5].

The rest of the bands in the region of 800-400 cm^{-1} (Fig. 1) can be attributed to lattice vibrations. There are usually 3 or 4 bands in all the samples of the whole Co-Al series. Although Mascolo and Marino [6] questioned the hydrotalcite structure for cation ratios higher than 3/1, the synthesized samples with M^{2+}/M^{3+}=4/1 or 5/1 cation ratios give the same hydrotalcite pattern (Table 1) and hence are also layer hydroxides. IR spectra are not sensitive to the cation subsitution and distribution.

3.2. IR data combined with X-ray powder analyses of calcined Co-Al hydrotalcite

After calcination at 723 K, all the Co-Al hydrotalcites show a spinel-like structure Co_2AlO_4 and Co_3O_4 (shown in Table 1). For the samples with Co/Al = 0.5 and 1.0, a poorly crystallized spinel-like phase was identified by XRD for the excess of aluminum content. Aluminum oxide could be amorphous. When Co/Al ratio equals to 3.0, the calcined hydrotalcite has sharper refraction pattern than the others, that illustrates a better crystallinity under such cobalt-aluminum ratio.

Figure 2 shows the variation trend of IR spectra after all the Co-Al hydrotalcites were calcined at 723K for 5 hours. The peaks at 1020, 860 and 800 cm^{-1} have gone. This implies easy elimination of molecular water. However, all the calcined hydrotalcites retained the absorption bands at around 3500cm^{-1}, 1600 cm^{-1}, and 1380cm^{-1}. As indicated in Fig. 3, further increase of calcination temperature up to 823 K made the broad band at 3400-3600 $cm^{-1}$and the band at 1380 cm^{-1} weaker, while the band at 1600 cm^{-1} persisted. This peak might have its origin from the moisture water during KBr pellet preparation.

Table 1 gives conversions of N_2O to N_2 and O_2 with calcined cobalt-aluminum hydrotalcite catalysts having varied ratios of cobalt and aluminum cations. The Co/Al ratio varied from 0.5 to 5.0 for decomposing N_2O. We obtained the best result at Co/Al = 3.0 which exhibits a N_2O conversion rate of 84.9% at 673 K with a space velocity of 15000h^{-1}.

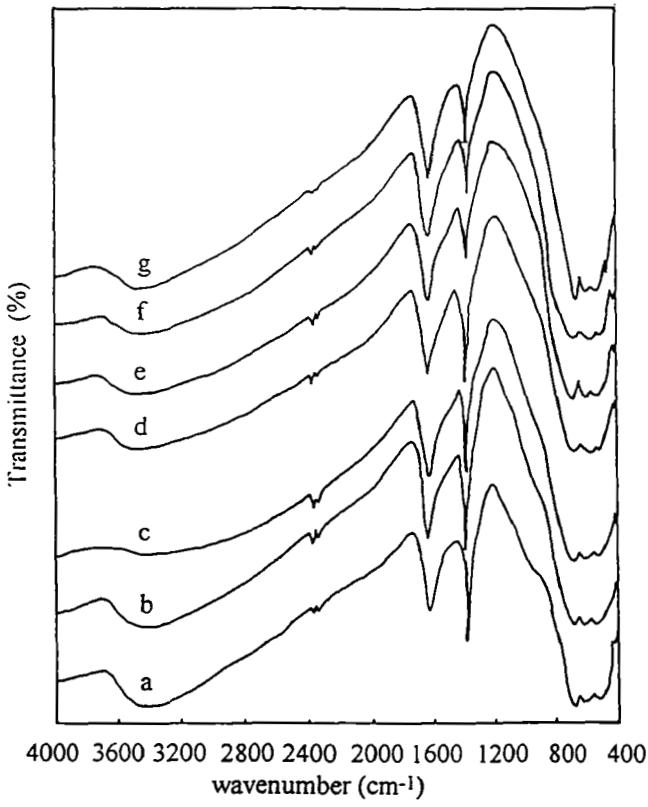

Fig. 3 IR spectra of Co-Al hydrotalcite (Co/Al = 3.0) under different calcination temperatures.
[a, b, c, d, e, f and g stand for 623K, 673K, 698K, 723K, 748K, 773K and 823K calcination temperature respectively.]

3.3. Catalyst activity of Co-Al hydrotalcite under different calcination temperatures (Co/Al=3.0)

When the hydrotalcite samples (Co/Al = 3.0) are calcined in a temperature range 673~823K, the surface area of the catalyst samples decreased from 158.9 to 98.5 m^2/g (Table 2). The catalyst calcined at 723K has the best activity for N_2O decomposition (84.9%).

Table 2

Calcination temperatures of hydrotalcites (Co/Al = 3.0) and their catalytic activities for N_2O conversion*

Calcination temperature (K)	BET area (m^2/g)	N_2O conversion (%)
673	158.5	51.8
698	156.9	68.7
723	143.2	84.9
748	136.3	73.7
773	119.4	55.7
823	98.5	23.9

*Catalyst: 60-80 mesh; GHSV: 15000h^{-1}. Reaction temperature: 673K

As shown in Fig. 3, for the hydrotalcite (Co/Al = 3.0), the intensity of the absorption bands of OH (around 3500cm^{-1}) and carbonate (1380cm^{-1}) become weaker with an increase of calcination temperature. It implies more OH and carbonate in the hydrotalcite are decomposed at higher calcination temperatures.

3.4. Effect of incorporation of Cu on the Co-Al hydrotalcites

When Co is partially replaced by Cu (Co/Cu = 2.7/0.3), the resulting Co-Cu-Al-HT material (Co/Cu/Al = 2.7/0.3/1) still reveals hydrotalcite structure by XRD analysis. After standard thermal activation (calcined temperature is 723 K) to Co-Al-HT, the identified phase is spinel, which may include both Co_3O_4 and Co_2AlO_4. Regarding the Co-Cu-Al-HT material after thermal activation, we postulate a new compound $Cu_xCo_{3-x}O_4$ should be formed along with Co_2AlO_4, because no free CuO phase was found. As Co is partially replaced by Cu, the catalytic activity for N_2O decomposition increases from 84.9 to 94.9% at a reaction temperature of 673K and a space velocity of 15000h^{-1}, although the surface area of catalyst decreases from 143.2 to 91.5 m^2/g.

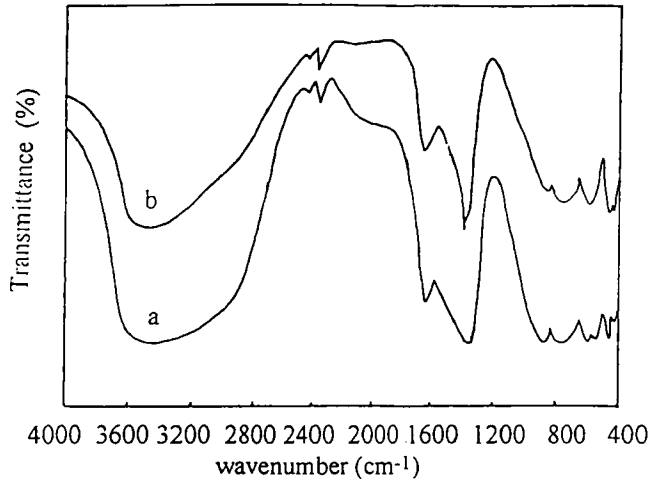

Fig. 4 Comparison of the IR spectra of uncalcined Co-Al and Co-Cu-Al hydrotalcites.

[a and b stand for Co/Al = 3.0, Co/Cu/Al = 2.7/0.3/1 hydrotalcite respectively.]

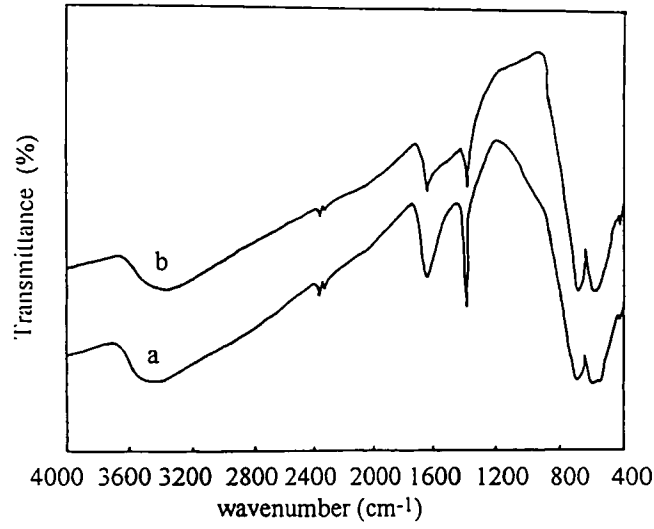

Fig. 5 Comparison of the IR spectra of calcined Co-Al and Co-Cu-Al hydrotalcites.

[a and b stand for Co/Al = 3.0, Co/Cu/Al = 2.7/0.3/1 calcined hydrotalcite respectively; Calcination temperature: 723K.]

Table 3

Calcination temperatures of hydrotalcites (Co/Cu/Al = 2.7/0.3/1) and their catalytic activities for N_2O decomposition*

Calcination temperature (K)	BET area (m^2/g)	N_2O conversion (%)
673	108.3	62.1
698	93.8	90.5
723	91.5	94.9
748	85.2	89.6
773	73.4	79.6

*Catalyst: 60-80 mesh: GHSV: 15000h^{-1}: Reaction temperature: 673K

That is to say, the appearance of the solid state $Cu_xCo_{3-x}O_4$ in calcined hydrotalcites improves the activity of catalyst by 10%.

Fig. 4 and 5 compare the variation of IR spectra between the hydrotalcite catalyst of Co/Al = 3.0 and Co/Cu/Al = 2.7/0.3/1. Before calcination, there is a shoulder peak around 1400cm^{-1} due to the addition of Cu to Co-Al-HT forming Co-Cu-Al-HT, which is attributed to a lowering of the symmetry of the carbonate in the hydrotalcite [5] (shown in Fig. 4). After calcination of Co-Cu-Al-HT, the absorption band at 660 cm^{-1} of Co_3O_4 shifts towards lower frequencies (650cm^{-1}, shown in Fig. 5). It suggests the formation of $Cu_xCo_{3-x}O_4$, that influences the Co-O bond strength.

3.5. IR spectra of Co-Cu-Al hydrotalcite under different calcination temperatures (Co/Cu/Al = 2.7/0.3/1)

We also tested the effect of calcination temperature on the catalytic activity of Co-Cu-Al calcined hydrotalcite (shown in Table 3).

Again with an increase of calcination temperature of the Co-Cu-Al hydrotalcites, the absorption bands of OH (around 3500cm^{-1}) and carbonate (1380cm^{-1}) becomes weaker (shown in Fig. 6).

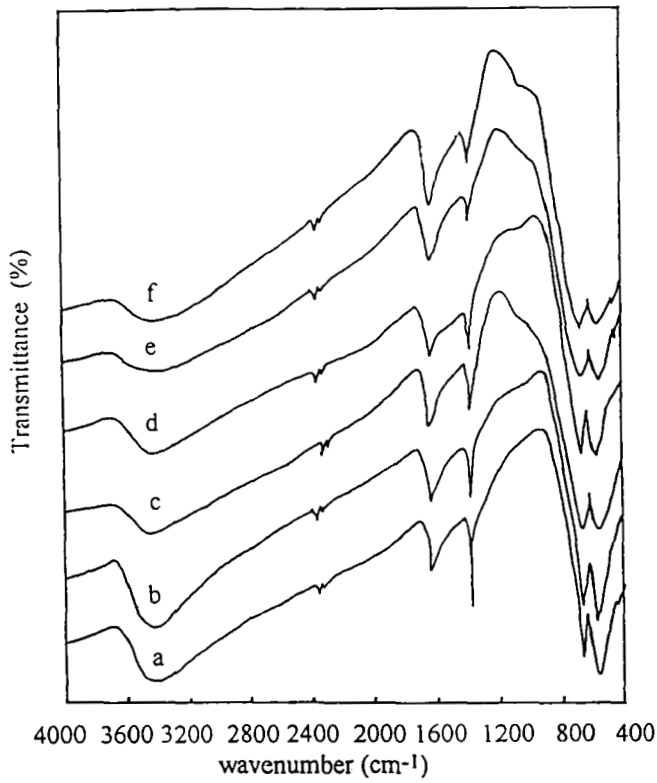

Fig. 6 IR spectra of Co-Cu-Al hydrotalcite (Co/Cu/Al = 2.7/0.3/1) under different calcination temperatures.
[a, b, c, d, e and f stand for 623K, 673K, 698K, 723K, 748K and 773K calcination temperature respectively.]

3.6. Effect of Co/Cu/Al ratio on Co-Cu-Al hydrotalcite catalyst

As shown in Table 4, with more Cu substituting Co in the hydrotalcite we found that malachite appears besides hydrotalcite phase before calcination. After calcination, malachite is converted into CuO phase, which appears besides spinel phases $Cu_xCo_{3-x}O_4$ and Co_2AlO_4. Upon a complete substitution of Co by Cu (Cu/Al = 3.0), only CuO phase was found by XRD. Aluminum oxide pattern could not be detected by

Table 4

Co/Cu/Al ratio in hydrotalcites and their catalytic activities for N_2O decomposition* after calcination at 723K

Co/Cu/Al ratio	Phases identified before calcination	Phases identified after calcination	BET area (m^2/g)	N_2O conversion (%)
2.7/0.3/1	hydrotalcite	Spinel	91.5	94.9
2.4/0.6/1	hydrotalcite	Spinel	81.9	75.6
2.1/0.9/1	hydrotalcite + malachite	Spinel + CuO	74.3	41.6
1.5/1.5/1	hydrotalcite + malachite	Spinel + CuO	71.0	20.9
0.9/2.1/1	hydrotalcite + malachite	Spinel + CuO	62.4	20.3
0.3/2.7/1	hydrotalcite + malachite	Spinel + CuO	60.2	20.9
0/3/1	hydrotalcite + malachite	CuO	46.5	21.4

*Catalyst: 60-80 mesh: GHSV: 15000h^{-1}; Reaction temperature: 673K: Spinel phases: $Cu_xCo_{3-x}O_4$ + Co_2AlO_4

XRD, probably due to its amorphous form. As the content of Cu in the hydrotalcite increased, the catalyst activity decreased rapidly until Co/Cu/Al = 1.5/1.5/1. For the hydrotalcite with a composition of Co/Cu/Al = 2.1/0.9/1, it has a lower catalytic activity than the sample of Co/Cu/Al = 2.7/0.3/1. It can be explained by the presence of CuO instead of the dominant spinel structure and by its smaller specific surface area.

Fig. 7 and 8 show the effect of Co/Cu/Al ratio on the IR spectra of Co-Cu-Al hydrotalcite catalysts. Before calcination, the intensity of the peak at 850-880cm^{-1} which corresponding to ν_2 vibration of the carbonate becomes stronger with an increment of Cu content in the Co-Cu-Al hydrotalcite. XRD analysis supports the change in IR spectra. As the molar ratio of Co/Cu/Al becomes 2.1/0.9/1, malachite phase can be identified besides the hydrotalcite phase.

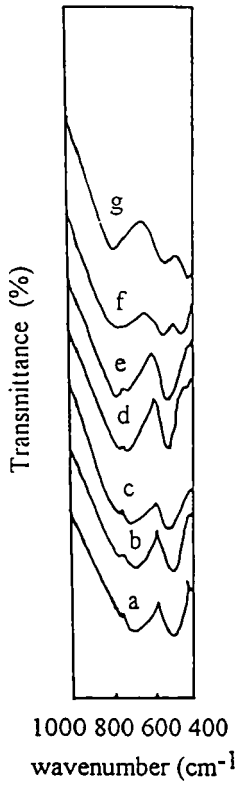

Fig. 7 IR spectra of uncalcined Co-Cu-Al hydrotalcites.
[a, b, c, d, e, f and g stand for Co/Cu/Al = 2.7/0.3/1, 2.4/0.6/1, 2.1/0.9/1, 1.5/1.5/1, 0.9/2.1/1, 0.3/2.7/1 and 0/3/1 hydrotalcite respectively.]

When all the Co-Cu-Al hydrotalcites are calcined at 723K for 5h, the major change in IR spectra occurs in the range of 400-800cm^{-1} corresponding to the lattice vibration of cation-oxygen. According to Sadlter standard IR spectra of inorganics, the strong and broad band at 440-580cm^{-1} and very weak band at 730cm^{-1} can be assigned to the lattice vibration of CuO. With more Cu incorporated for Co, the peak intensities of Co_3O_4 (660 and 570 cm^{-1}) become weaker, meanwhile the peak

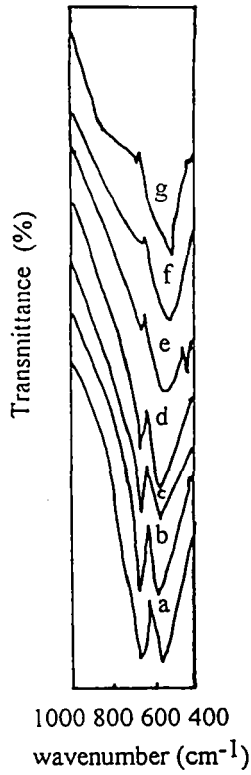

Fig. 8 IR spectra of calcined Co-Cu-Al hydrotalcites.
[a, b, c, d, e, f and g stand for Co/Cu/Al = 2.7/0.3/1, 2.4/0.6/1, 2.1/0.9/1, 1.5/1.5/1, 0.9/2.1/1, 0.3/2.7/1 and 0/3/1 hydrotalcite respectively; calcination temperature: 723K.]

intensities of CuO (440-580cm^{-1}) become stronger. When Cu/Al equals to 3.0, the IR spectra shown are the overlapping spectra of CuO and Al_2O_3 (Fig.8).

Acknowledgment

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