

## SYNTHESIS OF COBALT MIXED OXIDE DERIVED FROM HYDROTALCITE PRECURSOR FOR NO<sub>x</sub> STORAGE-REDUCTION

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### Abstract

Cobalt mixed oxide derived from hydrotalcite-like material was tested as a potential catalyst for NO<sub>x</sub> storage/reduction reaction. Co<sub>3.1</sub>Mg<sub>0.5</sub>Al<sub>1</sub> (CoHT) hydrotalcite-like compound was synthesized by the co-precipitation method and characterized by XRD, TGA, SEM, BET techniques. The calcination of CoHT at 450°C resulted in mixed oxide with high surface area 180m<sup>2</sup>/g. The specific surface area of prepared CoHT increases during the calcination with increasing temperature and reaches a maximum in the range 400-450°C, and then decreases.

The storage capacity for NO<sub>x</sub>, except composition, was dependent on the storage temperature. In general, more NO<sub>x</sub> was stored at a lower temperature (100°C) and than at a higher temperature (300-350°C). The storage/reduction mechanism and the function of Co in the mixed oxides are proposed and discussed. The role of cobalt is NO oxidation to NO<sub>2</sub> as well as NO/NO<sub>2</sub> capture in the form of nitrites and nitrates. Activation of the precursor, Co hydrotalcite, at a temperature of 750°C, leads to a significant reduction in the specific surface area and an increase in the mixed oxide particles. The result is a 50% reduction in storage capacity.

**Keywords:** Hydrotalcite-like materials; Co-Mg-Al mixed oxide catalyst; NO<sub>x</sub> storage-reduction catalyst; Cobalt, TPD.

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## 1. Introduction

Reducing the amount of NO<sub>x</sub> emissions from transport and industrial production is one of the major environmental problems. Climate change steps up efforts to reduce emission limits from all types of combustion processes. The tendency to use high fuel efficiency engines causes the engines must be operated in lean conditions with excess air. Under such conditions, conventional catalysts are less effective.

Reducing CO<sub>2</sub> emissions in the case of combustion engines leads to the use of a lean mixture and brings almost non-realizable requirements on catalytic NO<sub>x</sub> removal systems. At present, exhaust gas purification is a complex system which, with the use of a series of catalysts of various compositions and with the help of reducing agents, radically limits the emission of toxic compounds.

Two basic emission abatement technologies are used in automotive and power engineering:

- Selective catalytic reduction (SCR) by means of NH<sub>3</sub> or hydrocarbons,
- Lean NO<sub>x</sub> Trap (LNT, or referred to as NSR-store and NO<sub>x</sub> reduction technology)

Both, SCR and LNT NO<sub>x</sub> abatement technology have been investigated, and numbers of reviews have been published [1-4].

NSR after-treatment technology is cyclic. NO<sub>x</sub> emissions in the exhaust gas are trapped on the active sites of the catalyst surface during the lean phase of the cycle. The reduction of stored NO<sub>x</sub> to N<sub>2</sub> and restoring of the catalyst surface take place during the rich phase of the cycle [1]. Ba/Pt/Al<sub>2</sub>O<sub>3</sub> is considered the standard catalyst for this process. Under lean air to

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fuel condition, NO<sub>x</sub> reacts to form NO<sub>2</sub> over platinum particles followed by reaction with the barium compound to form BaNO<sub>3</sub>. The main problem of this catalyst composition is its sensitivity to sulphur compounds and low activity at low temperature.

Hydrotalcite has the chemical composition of Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O with a layered structure, it is interspersed with positively charged hydroxide [Mg<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> with layers of anions and hydrated water [(CO<sub>3</sub>)<sub>x/2</sub>·yH<sub>2</sub>O]<sup>x-</sup>. It is possible to prepare a synthetic compound with a crystal structure, with the following composition of the analogue M<sup>II</sup><sub>1-x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>A<sup>n-</sup><sub>x/n</sub>·yH<sub>2</sub>O where M<sup>II</sup> and M<sup>III</sup> are divalent and trivalent metal cation, and A<sup>n-</sup> means n valent anion and the value of x is powerful n-range 0.20 < x < 0.35. These compounds are in the literature referred to as hydrotalcites or layered double hydroxides or anionic clays. Hydrotalcite-like compounds are thermally stable material up to 305-400°C, at higher temperatures they are changed to mixed oxide or spinel [6].

The mixed oxides from hydrotalcite-like materials with cobalt were tested as catalyst or catalyst precursor in the NO/NO<sub>x</sub> removal process [7-17].

In this work, we have studied the possibility to use mixed oxides derived from hydrotalcite-like compounds as the alternative for NSR catalyst. The aim of the study was the influence of calcination temperature (450°C and 750°C) in cobalt containing HT-like precursor on the efficiency of NO<sub>x</sub> storing.

## 2. Experiments

### 2.1. Catalyst preparation

The Co-Mg/Al hydrotalcite-like compounds were synthesized by a co-precipitation method. An aqueous solution containing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in deionized water was added slowly under vigorous stirring into Na<sub>2</sub>CO<sub>3</sub> aqueous solution. Magnesium nitrate hexahydrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), cobalt nitrate hexahydrate Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, were obtained from Acros Organic. Sodium carbonate Na<sub>2</sub>CO<sub>3</sub> and sodium hydroxide (NaOH) formed Mikrochem Pezinok. All chemicals were of pure grade and used without further purification.

The co-precipitation was carried-out at a controlled pH of 11±0.2 by dropwise NaOH addition during the 4 hours. The co-precipitation was carry-out at vigorous stirring by Silverson L4L at 25°C. The resulting slurry was aged for 16 hours at 25°C without stirring. The precipitate was rinsed with deionized water to pH 7 separated by filtration and dried in air at 80°C. The as-prepared Co-HTICs were calcined at 450°C for 4 hr to derive the corresponding mixed oxide catalysts.

### 2.2. Catalyst characterization

SEM-pictures were obtained in TESLA BS 300 microscope in conjunction with TESCAN digitalizing unit.

The nature of the crystallographic phases was studied by XRD. The spectra were measured with Bragg-Brentano diffractometer Philips PW 1730/1050, using β-filtered CoKα radiation, 40kV/35mA in the range of 2° - 61° 2θ, step 0.02°.

The porous structure of the catalyst was studied by physical adsorption of nitrogen at -196°C using ASAP-2400 (Micromeritics). Before the analysis, samples were evacuated overnight at a chosen temperature from 150°C to 650°C under the vacuum of 2 Pa. Specific surface area S<sub>BET</sub> was obtained using conventional BET isotherm (p/p<sub>0</sub> = 0.05 - 0.3). Pore size distributions were calculated by standard BJH method from desorption isotherms. Total pore volume was determined from volume adsorbed at a relative pressure of p/p<sub>0</sub> = 0.99.

Thermal decomposition of the hydrotalcite-like material has been studied using Perkin-Elmer DTA/TG 6300 equipment with 50 mg of sample, rate 10°C/min, flow 100 mL of N<sub>2</sub>/min.

Acidity was determined by TPD of ammonia in the range of 220-550°C after activation at 500°C in the flow of helium. Basicity was determined by TPD of CO<sub>2</sub> in the range of 25-450°C after activation at 450°C in the flow of helium.

### 2.3. NO adsorption/thermal desorption experiments

Thermal NO<sub>x</sub> adsorption experiments were carried out in a SS flow reactor (i.d. = 30 mm and  $L = 1000$  mm) using 5 g of oxide catalyst (20–40 mesh powder) at the pressure 50kPa. The temperature in the catalyst bed was measured by a K-type thermocouple located in a SS capillary immersed in the catalyst bed. Oxide catalyst was pre-treated in a gas flow of O<sub>2</sub>/N<sub>2</sub> (8% O<sub>2</sub> by volume) at 500°C at a constant gas volume space velocity of ca. 24,000–31,000 mL/g.hr for 1 hr and then cooled to the experimental temperature (100, 200 or 300°C). When the temperature had stabilized at the desired temperature, 660µg/L NO in nitrogen and 8% O<sub>2</sub> in N<sub>2</sub> was introduced at a rate of 2,300 mL/min for 60–120 min for thermal NO<sub>x</sub> adsorption. Concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub> from the reactor outlet were monitored by a chemiluminescence-NO<sub>2</sub>, and NO<sub>x</sub> analyzer (Rosemount model 951A or Horiba PG 350). All gasses were introduced into the reactor through mass flow controllers (Bronkhorst).

After the thermal NO<sub>x</sub> adsorption, the flowing gas was switched to pure N<sub>2</sub> (rate = 500 mL/min, gas volume space velocity 30,000 hr<sup>-1</sup>) to flush the oxide catalyst for 20 min and remove the weakly adsorbed species at the adsorption temperature. The oxide catalyst was then cooled to 100°C. The temperature programmed desorption (TPD) was then conducted by heating the sample from 100 to 600°C at a ramp of 6°C/min with N<sub>2</sub> flowing at a rate of 2 200 mL/min. Concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub> from the reactor outlet were monitored by a chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer, and the adsorbed NO<sub>x</sub> amount was thus calculated.

### 3. Results and discussions

The chemical composition of the calcined hydrotalcites is comparatively shown in Table 1. The chemical composition of the samples of mixed oxide was determined by AAS after sample dissolution in hydrochloric acid (36%). The chemical composition of the samples was measured by atomic absorption with an iCE 3500 AASpectro Dual Varian EspectrAA-10 plus system (Thermo Scientific). The average error of the determination was 3% rel.

Table 1 Chemical composition characterization of mixed oxide catalysts

	Molar ratio	Cation concentration, % wt.		
		Co	Mg	Al
CoHT1	Co/Mg/Al=53/17/30	46.9	4.1	10.1
CoHT2	Co/Mg/Al=48/19/33	37.5	7.0	15.3

#### 3.1. Transformation of hydrotalcite to mixed oxides

The process of thermal decomposition of hydrotalcite to mixed oxides was monitored by TG/DTA analysis. The thermal decomposition of CoHT1 and CoHT2 samples are shown in Figures 1 and 2. Thermal decomposition of CoHTs consists of two phases. The first endothermic phase of decomposition took place in the temperature range 150–250°C. Loss of sample weight was associated mainly with the release of the interlayer and weakly adsorbed water molecules. The dehydration process is associated with a change in the layered structure of hydrotalcite as documented by XRD analysis.

The temperature range of the first hydrotalcite decomposition phase depends on the structure of the hydroxyl layer. Samples with a higher Al/Mg ratio have a maximum peak of 1 at 20–30°C higher (Table 2).

During the second decomposition phase of hydrotalcite, dehydroxylation of the brucite-like structure and interlayer anions occurs. The leakage of water and CO<sub>2</sub> molecules is observed at temperatures above 250°C as a sharp peak on the DTG curve. Maximum peak 2 is similarly dependent on the Al/Mg ratio.

Tab. 2. Thermal decomposition of CoHT catalyst

Sample	CoHT1	CoHT2
Maxima 1, °C	180	210
Maxima 2, °C	260	320

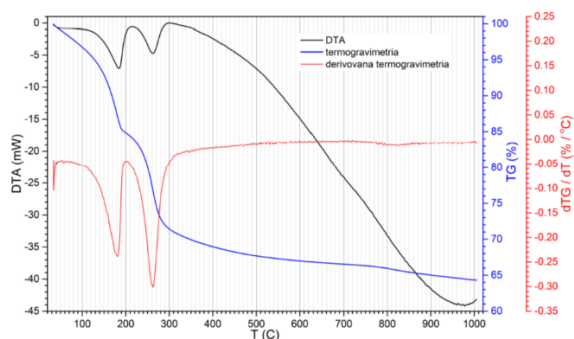


Fig. 1. DTA/TG pattern of CoHT1 sample

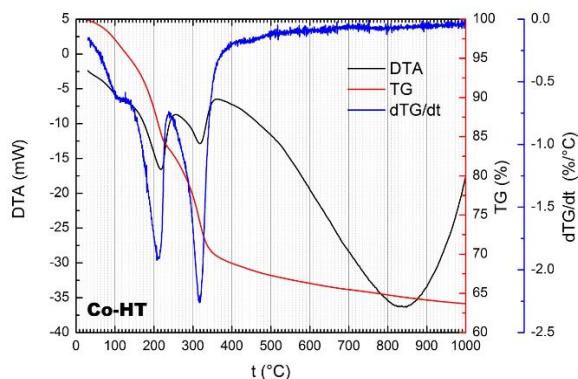


Fig. 2. DTA/TG pattern of CoHT2 sample

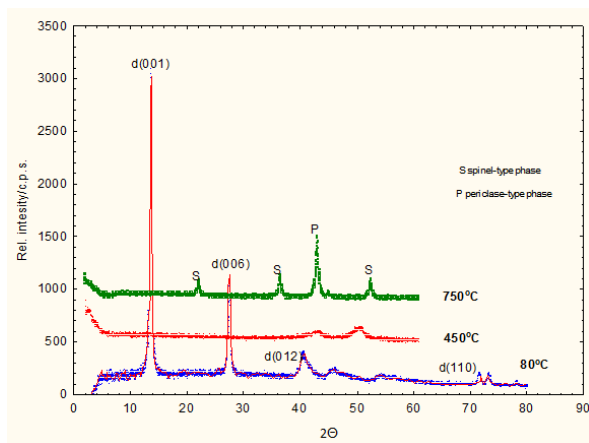


Fig. 3. Powder XRD patterns of Co co-precipitated hydrotalcite-like materials before and after calcination

XRD analysis of Co hydrotalcites showed virtually the same hydrotalcite structure of the prepared and dried basic samples. The un-calcined samples of CoHT show typical X-ray diffractogram (Fig.3) with the peaks at  $2\theta=13.6, 27.4$  corresponding to the (003) and (006) crystal planes. The broad diffraction peaks at  $2\theta=40.4, 45.9, 71.5, 73.4$  are characteristic poly-type hydrotalcites.

The samples maintain the hydrotalcite structure up to  $150^\circ\text{C}$ . At the annealing temperature of  $450^\circ\text{C}$ , the samples had low crystallinity. After calcination at  $650^\circ\text{C}$ , it can be observed mixed oxide structure; spinel-type phase and periclase like oxide.

The samples of hydrotalcites were calcined in the temperature range of  $150\text{--}750^\circ\text{C}$ , and adsorption isotherms were measured. The surface area  $S_{\text{BET}}$  and pore size distribution were calculated.

The shapes of adsorption isotherms of both as-synthesized samples of Co-hydrotalcites, degassed in measured burettes at  $150^\circ\text{C}$ , are similar, showing hysteresis loops at higher relative pressures. High nitrogen volume uptake starts at relative pressure over 0.90 for a sample of CoHT1, while for CoHT2 starts at relative pressure over about 0.80. This difference reflects in little different pore-size distributions in the wide-mesoporous range – for sample CoHT2 about 12 nm, and for CoHT1 pore diameter achieves even 30 nm.

As it is seen from Figs. 4 and 6, shapes of adsorption isotherms stay practically unchanged after thermal treatment up to  $750^\circ\text{C}$ , even if the crystalline structure according to XRD analysis radically changes. Similarly, pore size distributions remain similar – for CoHT1 about 30 nm, and for CoHT2 about 12.5 nm; only at highest temperature  $750^\circ\text{C}$  pore-size shifts to a little higher size.

Table 3. Texture and acid-base properties of prepared mixed oxides ( $450^\circ\text{C}$ )

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_a$ ( $\text{cm}_3/\text{g}$ )	$D_p$ (nm)	Acidity ( $\text{mmolNH}_3/\text{g}$ )	Basicity ( $\text{mmolCO}_2/\text{g}$ )
CoHT1	171	0.595	30	0.07	0.09
CoHT2	189	0.389	12.5	0.06	0.13

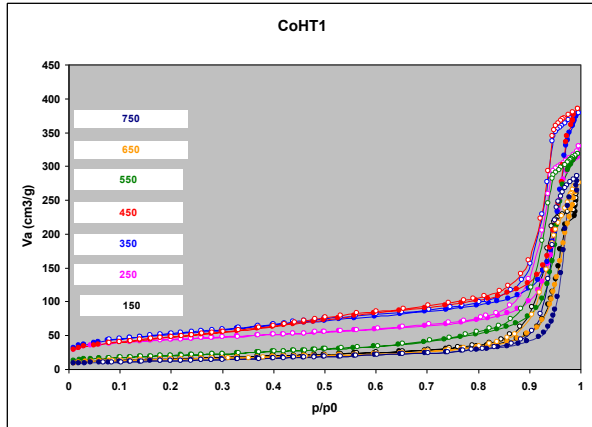


Fig. 4. Adsorption isotherms of CoHT1

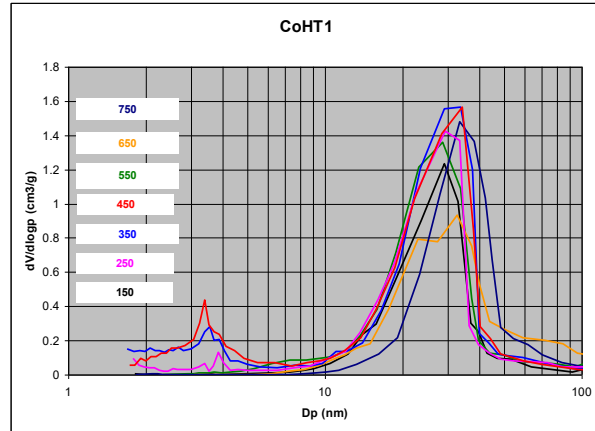


Fig. 5. Pore size distributions of CoHT1

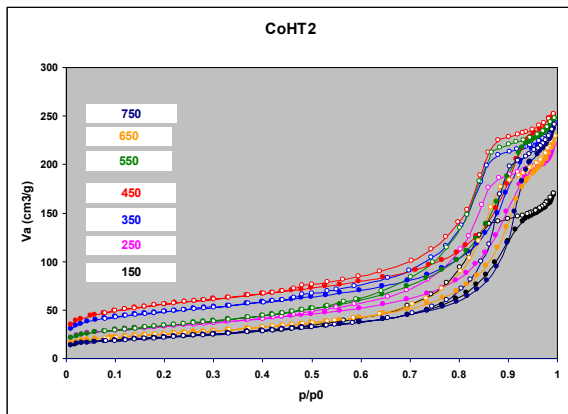


Fig.6. Adsorption isotherms of CoHT2

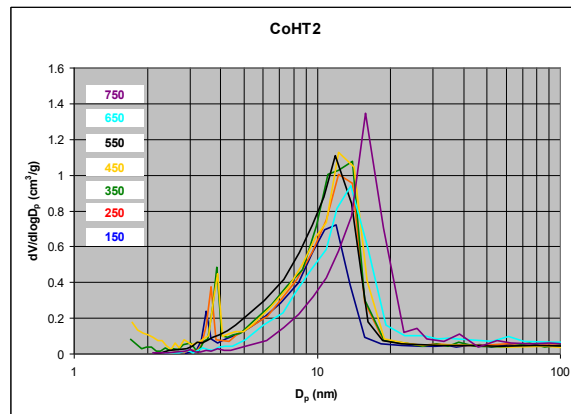
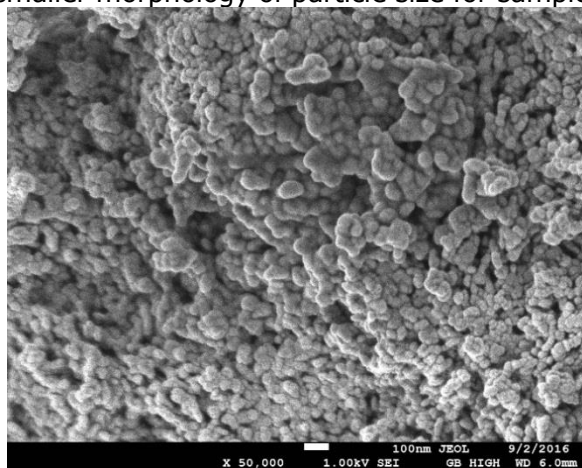
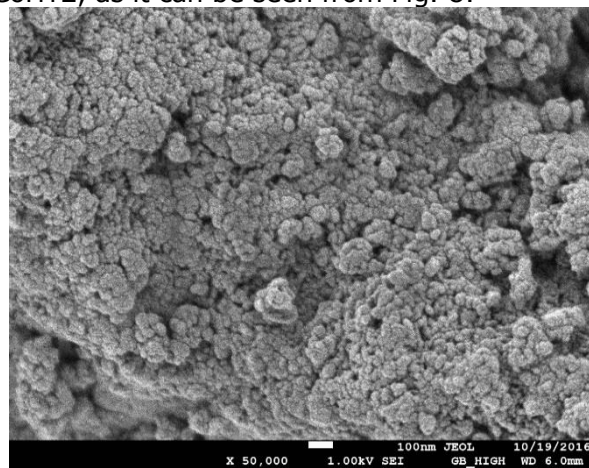


Fig.7. Pore size distributions of CoHT2

Texture properties after thermal treatment of 450°C (that was the activation temperature chosen for NSR experiments) are compared in Table 3. It is seen that sample CoHT1 with little smaller surface area (171 m<sup>2</sup>/g) has much higher total pore volume as a consequence of much higher pore size distribution. The differences in texture properties are probably connected with smaller morphology of particle size for sample CoHT2, as it can be seen from Fig. 8.



CoHT1



CoHT2

Fig. 8. Morphology of particle size of prepared Co-hydrothermalites at the magnification of 50.000

The acidity of both samples is similar – 0.07 mmol NH<sub>3</sub>/g for CoHT1 and 0.06 mmol NH<sub>3</sub>/g for CoHT2, but basicity for sample CoHT2 is about 45 % higher than for sample CoHT1 (0.13 against 0.09 mmol CO<sub>2</sub>/g)

### 3.2. NO adsorption/desorption on mixed oxide catalyst

The isothermal tests with the catalyst were carried out in the lean atmosphere (660µg/L NO and 4.19. % O<sub>2</sub> balanced by nitrogen) during the 60 and 120 minutes. The total gas flow was 2.1 L/min with corresponding gas hourly space velocity (GHSV) 23 194 L/g.h.

In particular, the following parameters were evaluated in the sorption process: NSE -the NO<sub>x</sub> storage efficiency in %, the NSC sorption capacity expressed as mg NO<sub>x</sub> / g of catalyst (NO<sub>x</sub> storage capacity), and NO to NO<sub>2</sub> conversion (%). Parameters are defined as follows:

$$NSC = \frac{\int_0^t NOx_{in} - NOx_{out} dt}{m_{cat}}$$

where:  $m_{cat}$  is the catalyst weight in g, NO<sub>x</sub> is the NO<sub>x</sub> concentration in mg and t = 60 minutes (120 min).

$$NSE = \left( 1 - \frac{\int_0^t (NOx_{out}) dt}{\int_0^t NOx_{in}} \right) * 100$$

For NO/O<sub>x</sub> adsorption desorption tests, two catalysts prepared from CoHT2 hydrotalcite were calcined at 450°C (CoHT2-450) and at 750°C (CoHT2-750).

The NO<sub>x</sub> storage properties were evaluated at the temperature ranges 100°C to 450°C under lean conditions. NO<sub>x</sub> storage efficiency (NSE) is defined as the amount of NO/NO<sub>x</sub> stored during the lean phase divided by the total amount NO/NO<sub>x</sub> supplied to the total catalyst layer. The results of the adsorption experiments are summarized in Table 4. In Table 5 is the cumulative amount of NO/NO<sub>x</sub> stores at the different adsorption temperature in mg NO<sub>x</sub>/g catalyst.

Table 4. NSE (%) at different adsorption temperatures and lean conditions

Time (min)	CoHT2-450				CoHT2-750			CoHT2-450 CO <sub>2</sub>	CoHT2-750 CO <sub>2</sub>
	100°C	200°C	300°C	450°C	100°C	200°C	300°C	350°C	350°C
1	92.2	96.1	95.8	91.8	44.2	22.8	14	94.5	23
5	89.3	93.8	91.7	88.1	51.9	31.2	42	90.4	43.5
10	89.9	93.5	90.8	80.3	52.9	35.2	57.2	89.9	44.6
30	82.6	84.1	87.1	57.5	48.3	30.6	46.6	84.4	37.0
60	68.8	69.0	81.1	-	40.5	23.1	34.1	74.9	28.3
90	54.9	57.5	-	-	35.1	19.2	25.9	61.3	22.6
120	45.3	49.1	-	-	31.2	16.3	20.8	50.6	-

Table 5. NO<sub>x</sub> storage capacities (NSC) tested at different temperatures

Catalyst	100°C	200°C	300°C	350°C	400°C	450°C
CoHT2-450	6.2	5.8	7.9	8.2	8.2	3.3
CoHT2-750	6.8	3.6	4.4	5.1	4.2	1.2
CoHT-450 CO <sub>2</sub>	-	-	-	5.1	-	-
CoHT-750 CO <sub>2</sub>	-	-	-	2.5	-	-

Unit: mg NO/g<sub>cat</sub>

After switching the NO, O<sub>2</sub> and N<sub>2</sub> stream to the reactor, the NO<sub>x</sub> concentration at the reactor outlet is sharply reduced, followed by sequential NO/NO<sub>2</sub> trap at the active centers until equilibrium is reached. The time of total absorption is dependent on the amount of cata-

lyst and the absorption temperature. With increasing time the outlet NO<sub>x</sub> concentration increases. Co accelerates oxidation of NO and NO<sub>2</sub> is much better chemisorbed than NO. The maximum storage capacity of CoHT2-450 and CoHT2-750 catalyst was observed in the temperature region 350-400°C.

When the activation temperature of CoHT2 catalyst rises from 450°C to 750°C, NSE and NSC were radically reduced. The result of the higher activation temperature is the formation of a spinel phase, which has a higher crystallite size (18-20nm) than the MgO (12.5 nm) phase and increases the average size between the crystallites. The surface area and the pore volume of CoHT2 catalyst decrease with increasing the temperature of activation (from 189 m<sup>2</sup>/g to 89.4 m<sup>2</sup>/g cat).

At a temperature of 100°C in the initial phase, chemisorption was almost complete; then the NO/NO<sub>x</sub> concentration rises until equilibrium was reached. The NO/NO<sub>x</sub> concentration was always lower than the NO input concentration.

At the chemisorption of NO above 300°C, there is a very different gas composition at the outlet of the reactor. Compared to the sorption temperature at 100°C, the NO<sub>2</sub> concentration increases significantly, and the NO concentration decreases. These changes in NO and NO<sub>2</sub> concentrations are due to the oxidation of NO to NO<sub>2</sub> by the Co component of the catalyst. This dependence is the same for both the catalyst activation temperature of 450°C and 750°C. The adsorption capacity of the CoHT2-450 catalyst was maximal in the temperature range of 300-400°C. In the case of the CoHT2-750 catalyst, the maximum adsorption capacity was at 100°C.

The desorption profiles of NO<sub>x</sub> with storage at 100, 200, 300, 350, 400°C are shown in Figures 9 and 10.

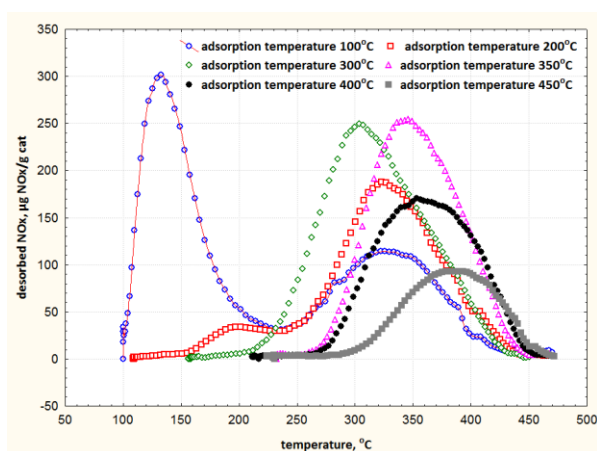


Fig. 9. NO<sub>x</sub>-TPD profiles of CoHT2-450 catalyst after chemisorption NO/O<sub>2</sub>/N<sub>2</sub> at different temperatures

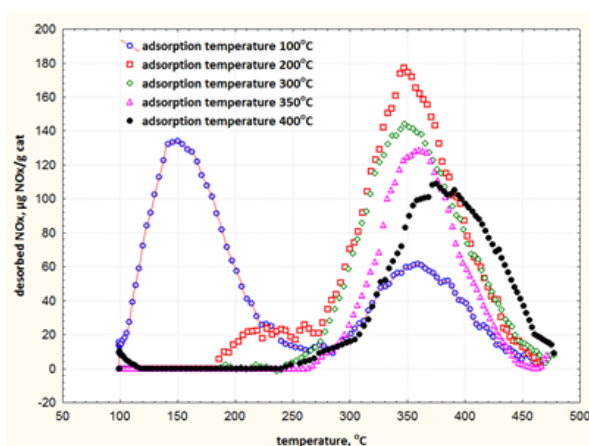


Fig. 10. NO<sub>x</sub>-TPD profiles of CoHT2-750 catalyst after chemisorption NO/O<sub>2</sub>/N<sub>2</sub> at different temperatures

Oxidation of NO to NO<sub>2</sub> at temperatures of 100-200°C was very limited, maximum oxidation conversion was in the range of 300-350°C and decreased by further increase of the temperature. Co oxide is responsible for the oxidation of NO to NO<sub>2</sub> and thus effective chemisorption to nitrites and nitrates. TPD experiments have confirmed that there are several types of active centers on the catalyst surface that are responsible for NO/NO<sub>2</sub> trapping. There are at least two types of centers with different reactivity on the catalyst surface.

NO desorption takes place on the catalyst CoHT 2-450 at 100°C in two temperature regions. Desorption in the 100-300°C temperature range with weakly bound nitrites predominated and ratio DeNO<sub>xL</sub>/DeNO<sub>xH</sub> was 1.72. At higher NO adsorption temperatures, partial NO oxidation to NO<sub>2</sub> and also nitrite to nitrate oxidation occurred. Ratio NO<sub>2</sub>/NO at 300°C was 22.3%, but at 400°C was only 3.6%.

Table 6. Progress of NO<sub>x</sub> desorption

catalyst	desorption area		DeNO <sub>xL</sub> /DeNO <sub>xH</sub> ratio			
	Low temperature area	High temperature area	100°C	200°C	300°C	400°C
CoHT2-450	100-300	300-450	1.72	0.12	0.07	0.01
CoHT2-750	100-250	250-450	0.62	0.06	0.03	0.01

The presence of CO<sub>2</sub> (17.4 vol.) in the NO/N<sub>2</sub>/O<sub>2</sub> mixture (5.5% vol.) had only a minor effect in chemisorption on CoHT2-450 at 300°C and caused only a 10% reduction in adsorption capacity. However, it had a significant impact on the NO<sub>2</sub> concentration in the desorption output stream, which increased by 60%. This can be explained by blocking strong base centers to produce more stable carbonates and by decomposing less stable nitrites and nitrates bound on weaker base centers. In the case of the CoHT2-750 catalyst, the presence of CO<sub>2</sub> had a dramatic effect on the reduction of adsorption capacity by 45%.

#### 4. Conclusions

Co-Mg/Al mixed oxides were prepared by co-precipitation technique at pH 11 and subsequent calcination on static air at the two different temperatures.

Prepared Co mixed oxides were tested as NSR catalysts. The catalyst activation temperature has been found to have a substantial effect on the catalyst surface area and storage capacity. NSR Co-catalysts chemisorb NO through nitrite route as the main NO/NO<sub>x</sub> capture mechanism. The Co mixed oxides also have a performance for NO direct decomposition to N<sub>2</sub> during the chemisorption phase.

#### Acknowledgment

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