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Rare earth metal modified alumina-supported copper cobaltite catalysts in reduction of NO with CO

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The effect of low loading rare earth metal addition (RE= La, Ce, Nd and Gd) to alumina supported copper-cobalt spinel oxide on the catalysts efficiency in NO reduction with CO was investigated. Samples RE/CuCo/Al (RE= La, Ce, Nd and Gd) were prepared by vacuum- evaporation. The rare earth modified as well as their "parent" catalysts were characterized by XRD, XPS, AAS, SEM-EDS, BET analysis. The catalytic experiments were carried out in catalytic flow apparatus in an isothermal flow reactor in the temperature range 20–500°C. It was found that the modification of alumina supported copper- cobalt spinel with rare earths (RE= La, Ce, Nd and Gd) influenced in different ways on the catalytic activity in NO reduction with CO depending on the temperature. For temperatures up to 100°C La has the most positive effect while at temperatures above 250°C Gd is the most proper modifier. Nd is not convenient for catalyst improvement in this reaction.

Keywords: rare earth, catalyst, modification, NO reduction with CO.

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INTRODUCTION

Exhaust gases containing nitrogen oxides from stationary and mobile combustion sources cause a variety of environmentally harmful effects. NOx removal from these gases still remains one of major challenges in the area of environmental catalysis [1-3]. The most common approach is the reaction with residual reductors (unburned or partially burned hydrocarbons and CO) in the exhaust. Various catalysts have been extensively studied. It was found out that Cu-Co oxide spinels such as $Cu_xCo_{(3-x)}O_4$ [4] and $CuCo_2O_4/\gamma\text{-}Al_2O_3$ [5] are catalysts demonstrating high activity in the reduction of NO with CO.

The mixing of two different oxides offers an opportunity not only to improve the performance of the involved metal oxide but also to form new stable compounds that may lead to totally different physicochemical properties and catalytic behavior from the individual components. In order to improve the activity of copper-based catalysts for the SCR, some additives, such as Fe, Co, Ni, V, Mn, W, Mo, and Cr, were doped for the promotion of the copper species dispersion. The addition of certain promoters could enhance the catalytic performance of supported catalysts for the SCR of NOx with hydrocarbons [6]. Cerium oxide is a commonly used promoter in automotive three-way catalysts [7]. The rare earth oxides, although constituting a closely related group of compounds, exhibit a rich variety of characteristic behaviors and solid-state properties, including features that make them interesting subjects for catalytic studies [8].

In the present work we investigate the effect of low loading rare earth metal addition (RE= La, Ce, Nd and Gd) to alumina supported copper-cobalt spinel oxide on the catalysts efficiency in NO reduction with CO.

EXPERIMENTAL

Alumina supported copper cobaltite catalyst (CuCo/Al) was prepared preliminary according to [9] procedure. It has been established that after modification of the support with Cu^{2+} ions, the stoichiometric $CuCo_2O_4$ phase is formed, thus avoiding the "chromatographic effect". This catalyst was impregnated with 1wt. % La, Nd, Ce and Gd by nitrate solutions. The catalysts for the targeted research were obtained in a vacuum-evaporator and thermally treated at 500°C for 2 h. The samples RE/CuCo/Al (RE= La, Ce, Nd and Gd) were prepared.

The rare earth modified as well as their "parent" catalysts were characterized by XRD, XPS, SEM-EDS, AAS and BET analysis. The catalytic experiments were carried out in catalytic flow apparatus in an isothermal flow reactor in the

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temperature range 20–500^{o}C. After the catalytic test a temperature-programmed desorption (TPD) was carried. The transient response method was used to study the interaction of the gas phase with the catalyst surface. The transient response method [10] was used to study the interaction of the gas phase with the catalyst surface. The turnover frequency (TOF) values (converted NO per surface unit of RE = La, Nd, Ce and Gd metal) were calculated in order to evaluate the RE metal promotion on the studied catalysts:

$$\mathrm{TOF} = \frac{V \cdot C \cdot M \cdot \eta}{22.4 \cdot P \cdot A}$$

where V is space velocity (cm^3/h), C is inlet concentration of NO (vol.%), M is molecular mass of NO, η is a conversion of NO (%), P $_{\text{RE-}}$(g) is the active metal content and A is specific surface area (m^2/g).

RESULTS AND DISCUSSION

From XRD analysis (not presented here) no additional peaks due to rare earth oxides (REOs) (except CeO_2) were detected for the investigated samples. All diffraction peaks are relatively broad and reveal the fine crystalline nature of the support. The XRD data do not present a satisfactory picture for the phase composition of REOs, because the content of rare earths is quite low and the supported oxides are with a high dispersity.

Table 1 presents the results from AAS, SEM-EDS and BET specific surface areas. It is noticeable that the addition of rare earths does not affect substantially on the specific surface area values and their relative persistence reveals that the pores are not blocked or filled.

SEM-EDS analysis (Fig. 1) gives evidence for the availability of REOs on the surface as well as for the morphology of the synthesized samples. The Fig.1 presents the micrographs of the parent sample CuCo/Al and of two of the promoted - Ce/CuCo/Al and Gd/CuCo/Al catalysts. The RE promoted samples are more finely dispersed than the parent alumina supported copper-cobalt spinel. REOs phases are homogeneously distributed on the surface with average size of the particles of ~ 20 nm.

The catalytic results show that different REs affect in different ways on the activity of the alumina supported copper cobaltite (Fig. 2). The conversions both of NO and CO at 250^{o}C were close to 100% using La, Ce or Gd as dopants.

Table 1. AAS analysis, EDS elemental analysis and BET specific surface areas.

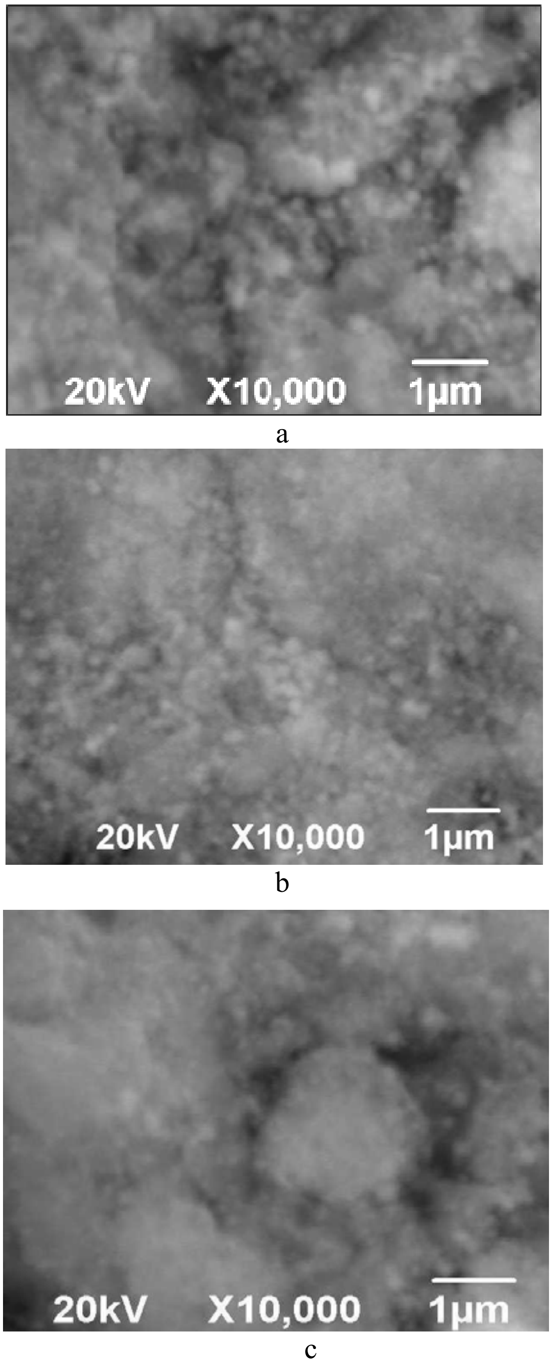
Sample	Cu, wt. %		Co, wt.%		RE, wt.%	S_{BET} m^2/g
	AAA	EDS	AAA	EDS	EDS	
CuCo/Al	11.92	37.07	14.20	8.36	-	157
Ce/CuCo/Al	11.92	38.06	14.20	9.66	0.91	155
Nd/CuCo/Al	11.92	40.06	14.20	10.05	1.10	144
La/CuCo/Al	11.92	37.35	14.20	9.23	1.10	143
Gd/CuCo/Al	11.92	21.10	14.20	18.04	1.21	152

The lowest catalytic activity was observed using Nd as a modifier, which exhibits lower activity than the mother catalyst in the whole temperature interval. The selectivity to N_2 depends on the temperature. For all catalysts it is almost 100% at temperatures higher than 200^{o}C. The calculated TOF values (Table 3) and Fig. 2 differentiate two temperature regions of activity also. For temperatures up to 200^{o}C the order of activity is:

La/CuCo/Al>Gd/CuCo/Al>Ce/CuCo/Al> CuCo/Al >Nd/CuCo/Al, at higher temperatures the order is: Gd/CuCo/Al>Ce/CuCo/Al>La/CuCo/Al> CuCo/Al > Nd/CuCo/Al.

TPD investigations show that the mechanisms of the interaction between NO and CO. It is evident that all samples have desorption peaks for NO (Fig.3). The desorptions present differences between the parent catalyst CuCo/Al and the RE modified ones. Only for CuCo/Al sample desorptions of NO and CO are registered, wherethese desorptions coincide in temperature. CO_2 desorptions are not detected. Hence, at lower temperatures the interaction on CuCo/Al proceeds via adsorbed species of NO and CO, evidenced by TPD, while on RE/CuCo/Al there is no clear indication for CO adsorption. The most intense at low temperature (80^{o}C) is the NO desorption of La/CuCo/Al which represents the catalysts with the highest activity at 100^{o}C. The most active catalysts at higher temperatures have two desorption NO peaks at 110 and 190^{o}C for Gd/CuCo/Al and at 160 and 330°C for Ce/CuCo/Al. These peaks represent probably two forms of NO adsorption.

A transient response method was applied to obtain information about the processes that occur on the surface of the studied catalysts and about the mechanism of the reduction of NO with CO. The differences in the curves reveal the different rate-controlling steps of the reaction over the catalysts.



a

b

c

Fig. 1. SEM micrographs of a) CuCo/Al, b) Ce/CuCo/Al and c) Gd/CuCo/Al.

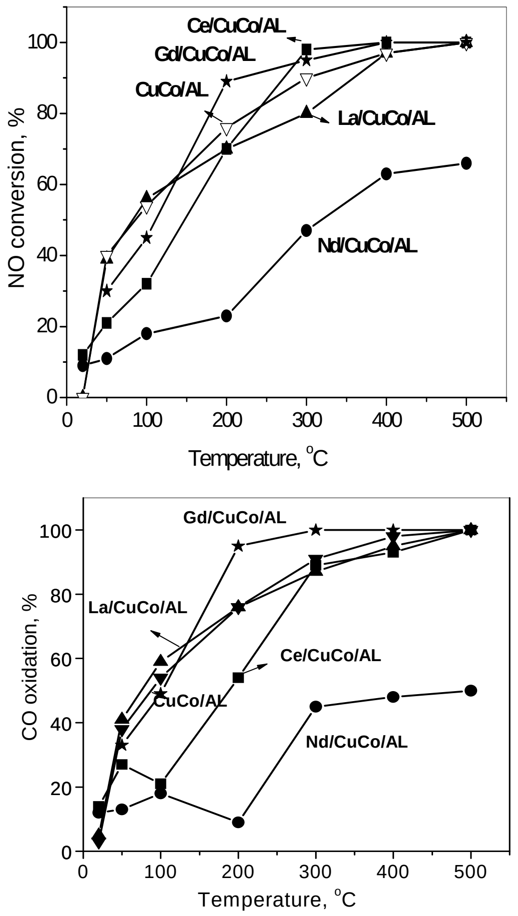


Fig. 2. Temperature dependence of the conversion degree of NO and CO on samples Gd/CuCo/Al, Ce/CuCo/Al, La/CuCo/Al, Nd/CuCo/Al and CuCo/Al.

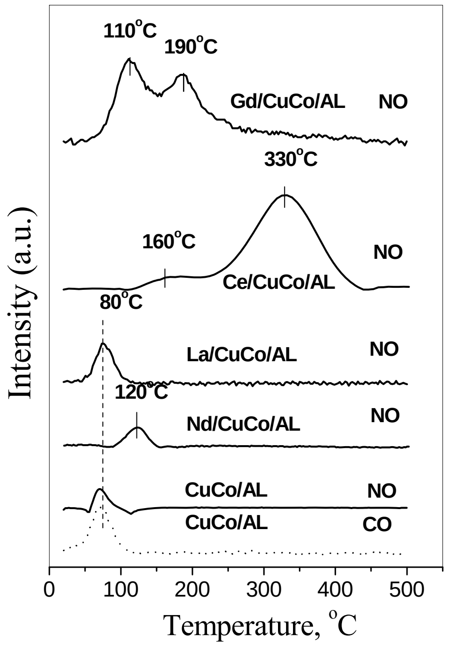


Fig. 3. TPD spectra of NO and CO for the investigated samples.

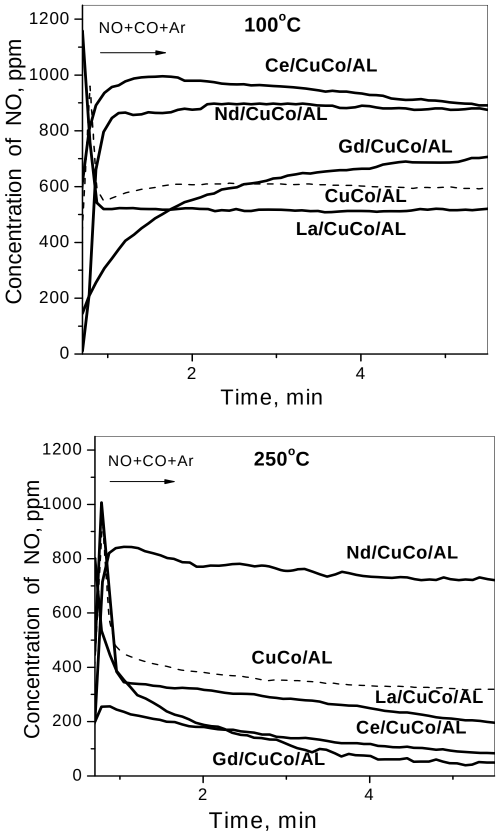


Fig. 4. Transient response curves of NO on Gd/CuCo/Al, Ce/CuCo/Al, La/CuCo/Al, Nd/CuCo/Al and CuCo/Al at 100 and 250°C.

The change in the rate-controlling step is associated with a change in the reaction mechanism. In Fig. 4 the transient response curves of reactant NO are presented at 100°C and 250°C. At 100°C the response curves for NO are of a monotonically growing type for Gd/CuCo/Al and of an instantaneous type at for Ce/CuCo/Al, La/CuCo/Al, Nd/CuCo/Al and CuCo/Al. The monotonically type response, according to Kobayashi's classification, indicates that the rate-limiting step in the reaction mechanism could be the surface reaction or desorption of the products. As desorption of the products is absent in the stop stage the surface reaction seems to be the rate-determining step. The instantaneous response deduces that the rate-limiting step could be the surface reaction or the adsorption of the reagents.

The transient curves for NO at 250°C for Gd/CuCo/Al and Ce/CuCo/Al are of the overshot type response, indicating that the rate-limiting step in the reaction mechanism could be creation or regeneration of the new catalytically active sites responsible for both reduction and decomposition of NO. The results coincide with the TPD spectra these samples that represent two desorption (low and high) peaks for both samples. This implies the change in the reaction mechanism for these catalysts that are the most active at temperatures above 250°C. The response curves show that depending on the temperature the catalytic reaction proceeds on various types of active centers.

CONCLUSION

The modification of alumina supported copper-cobalt spinel with rare earths (RE= La, Ce, Nd and Gd) influenced in different ways on the catalytic activity in NO reduction with CO depending on the temperature. For temperatures up to 100°C La has the most positive effect while at temperatures above 250°C Gd is the most proper modifier. Nd is not convenient for catalyst improvement in this reaction.

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НАНЕСЕНИ НА АЛУМИНИЕВ ОКСИД МОДИФИЦИРАНИ С РЕДКОЗЕМНИ МЕТАЛИ КАТАЛИЗАТОРИ ОТ МЕДЕН КОБАЛТИТ В РЕАКЦИЯТА НА РЕДУКЦИЯ НА NO С CO

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(Резюме)

Ефектът от малки добавки от редкоземни елементи (RE= La, Ce, Nd и Gd) върху нанесен на алуминиев оксид медно-кобалтов шпинелен оксид по отношение ефективността в редукцията на NO с CO беше изследван. Образците RE/CuCo/Al (RE= La, Ce, Nd и Gd) бяха приготвени чрез вакуум-изпарение. Модифицираните с редкоземни елементи катализатори, както и медно-кобалтовият катализатор бяха охарактеризирани с XRD, XPS, SEM-EDS, AAS и BET анализи. Каталитичните експерименти бяха проведени в поточна каталитична апаратура с изотермичен реактор в температурен интервал 20–500^{o}C. Намерено е, че модифицирането на нанесения на алуминиев оксид медно-кобалтов шпинел с редкоземни елементи (RE= La, Ce, Nd и Gd) влияе по различен начин върху каталитичната активност при редукцията на NO с CO в зависимост от температурата. За температури до 100^{o}C La притежава най-положителен ефект, докато при температури над 250^{o}C Gd е най-подходящият модификатор. Nd не е подходящ за подобряване на каталитичната активност при тази реакция.