

Effect of lanthanum on the activity and thermal stability of copper-cobalt oxide catalysts supported on alumina

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La-modified alumina-supported copper oxide and cobalt oxide catalysts were investigated. The catalyst samples were prepared by impregnation of supports (γ -Al₂O₃ or La-modified γ -Al₂O₃) with a mixed aqueous solution of Cu and Co nitrates. The samples were characterized by ICP analysis, X-ray powder diffraction (XRD) and BET method. The catalytic reduction of NO by CO and the catalytic oxidation of CO and C₆H₆ by O₂ were carried out over non-modified and La-modified catalysts. The modification of γ -Al₂O₃ support with La at a loading below 3 wt. % has a positive effect on the catalytic performance of supported Cu-Co oxide catalysts. Lanthanum plays a stabilizing role on the specific surface area of the carriers and Cu-Co oxide catalysts; the addition of La suppresses the α -transformation of the alumina support and its interaction with the active Cu-Co oxide phase to produce aluminates. The modification of the support with La prevents the intercalation of Cu ions into the γ -Al₂O₃ during the impregnation with Cu-Co nitrates. Thus, the active Cu-Co oxide spinel supported on La/Al₂O₃ has a higher Co:Cu ratio, which is close to that in the stoichiometric CuCo₂O₄ spinel. La-modified catalysts have higher activity in the NO+CO, CO+O₂ and C₆H₆+O₂ reactions, compared to the non-modified catalysts. Incorporation of La into the support does not change the energy level of catalytically active sites but rather increases the number of these sites.

Keywords: La-modified alumina, Cu-Co oxide spinel catalysts, NO reduction, oxidation of CO and C₆H₆ by O₂

1. INTRODUCTION

Transition metal oxides are active catalysts for a wide range of reactions for environmental protection such as NO reduction, CO and hydrocarbons (HC) oxidation [1]. On the other hand, lanthanum oxide exerts considerable influence on the thermal stabilization of alumina [2] and modification by La leads to a high catalytic activity in the CH₄ reforming with CO₂ [3]. It was found out [4] that Mn and Cu performance was better, when dispersed onto alumina in the presence of La and that La increased the insertion of copper into alumina. The addition of La₂O₃ promotes the dispersion of the active phase all over the alumina support [5-7], thus decreasing the degree of crystallinity and decreasing the particle size. Barrera *et al.* [8] established that the La₂O₃ in the Pd/Al-La catalysts, prepared by the sol-gel method, promotes the oxidation of Pd and dissociation of NO at low temperatures favoring the formation of N₂. A lanthanum-promoted Pd/Al₂O₃ catalyst [9] shows a higher activity for the hydrogenation of phenol with H₂ than non-promoted Pd/Al₂O₃ catalyst and the dispersion of Pd could strongly

depend on the dispersion of lanthanum on Al₂O₃. It was found out that Cu-Co oxide spinels such as Cu_xCo_(3-x)O₄ [10, 11] and CuCo₂O₄/ γ -Al₂O₃ [12] are catalysts demonstrating high activity in the reduction of NO with CO. The presence of copper ions in the impregnation solution sharply lowers the adsorption capacity of alumina with respect to the cobalt ion from solution in case of depositing Cu-Co oxide spinels onto γ -Al₂O₃ [13]. As a result of this the so called "chromatographic effect" appears, which is due to the stronger selective adsorption of one of the ions in the solution on the surface of the support.

The purpose of the present work was to investigate the process of copper oxide and cobalt oxide deposition on alumina and on La-modified alumina as well as the catalytic reactions of NO reduction with CO and oxidation of CO and C₆H₆ by O₂ on these catalysts.

2. EXPERIMENTAL

Catalyst preparation

The support γ -Al₂O₃ (Rhone-Poulenc) has a specific surface area of 260 m²g⁻¹. The La-modified samples were prepared by impregnation of γ -Al₂O₃

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(sieve fraction with grain size 0.3-0.6 mm) with an aqueous solution of lanthanum nitrate (the content of La was 1.31 g La/100 cm³). The catalyst samples were prepared by impregnation of the supports (γ -Al₂O₃ or La-modified γ -Al₂O₃) with a mixed aqueous solution of the nitrates of Cu and Co. The concentrations used were (7.04 g Cu + 13.98 g Co)/100 cm³ in order to ensure a ratio Co:Cu = 1.99, which is close to the weight ratio Co:Cu = 1.85 for the stoichiometric CuCo₂O₄ spinel. Separate samples of the so prepared catalysts were dried in air for 2 h at 120°C and calcined for 3h at 550°C and at 1050°C. In this way, the following samples were obtained:

A_550, γ -Al₂O₃ → calcination at 550°C;

A_1050, γ -Al₂O₃ → calcination at 1050°C;

LA_550, obtained by impregnation of γ -Al₂O₃ with aqueous solution of lanthanum nitrate → calcination at 550°C;

LA_1050, obtained by impregnation of γ -Al₂O₃ with aqueous solution of lanthanum nitrate → calcination at 1050°C;

SA_550, obtained by simultaneous impregnation of γ -Al₂O₃ with copper and cobalt present in the impregnating solutions → calcination at 550°C;

SA_1050, obtained by simultaneous impregnation of γ -Al₂O₃ with copper and cobalt present in the impregnating solutions → calcination at 1050°C;

SLA_550, obtained by impregnation of γ -Al₂O₃ with aqueous solution of lanthanum nitrate → calcination at 550°C → impregnation with copper and cobalt present in the impregnating solutions → calcination at 550°C;

SLA_1050, obtained by impregnation of γ -Al₂O₃ with aqueous solution of lanthanum nitrate → calcination at 1050°C → impregnation with copper and cobalt present in the impregnating solutions → calcination at 1050°C.

Catalyst characterization

The La, Cu and Co contents in the impregnating solutions and in the synthesized catalysts were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) on a spectral analyzer JY38 (Jobin Yvon, France).

X-ray diffraction (XRD) data were obtained using a Bruker D8 Advance diffractometer with Cu-K α radiation and SolX detector.

The texture characteristics were determined by low-temperature (77.4 K) nitrogen adsorption in a conventional volumetric apparatus. The specific

surface area was evaluated by the single-point BET method.

Catalytic activity measurements

The catalytic activity experiments were carried out in a continuous flow reactor described previously [10]. The NO reduction with CO was investigated in the temperature range 25-500°C. The catalytic activity tests were performed with a NO+CO+Ar feed gaseous mixture, containing 1200 ppm NO and 1200 ppm CO. Argon was used as a carrier gas at a total gaseous hourly space velocity of 433 cm³min⁻¹ (GHSV 33 000 h⁻¹). A 1 cm³ sample of a catalyst (0.3 - 0.6 mm sieve fraction) was charged in the reactor representing a quartz tube of internal diameter d=10 mm. The concentrations of NO and CO were continuously measured by gas analyzers. The concentrations of NO and CO in the converted mixture were controlled using the UNOR 5 –Maihak and the CO₂ – using the Infracal 2106 gas analyzer. The concentrations of NO, CO and CO₂ were continuously measured by gas analyzers and the data were collected on a CSY-10 personal data station. Specord 75 IR spectrophotometer with a 1 m folded path gas cell (Specac) was used for determination of the N₂O content at the outlet. The N₂ concentration in the outlet gas was determined on the basis of the material balance with respect to NO consumption. Before the catalytic activity test, the catalysts were treated thermally in an Ar flow at 500°C for 1 h. Afterwards the catalyst bed temperature was decreased down to room temperature. The chronology of this set of experiments involves a reaction step (NO+CO+Ar) and an isothermal desorption step (Ar flow) carried out at successively higher and higher temperatures in the range from 50 to 500°C. Temperature programmed reaction (TPR) experiments with NO+CO+Ar feed mixture were carried out on the same catalytic apparatus at a heating rate of 13°C/min in an Ar flow (440 cm³ min⁻¹) continuously fed into the reactor. The catalytic tests for CO+O₂ and C₆H₆+O₂ reactions were performed in an analogous flow apparatus at a carrier gas (Ar flow) space velocity of 20 000 h⁻¹. The inlet and the outlet concentrations of CO and CO₂ were controlled on an Infracal 2106, NDIR gas analyzer. A Pye Unicam (UK) gas chromatograph with a FID detector was used for the C₆H₆ converted mixture analysis. A dosing pump Ismatex MS2/6 (Switzerland) was utilized to control the feed concentrations of CO and C₆H₆.

Table 1. Chemical composition, BET specific surface areas and phase composition of the samples.

Sample	Metal content (wt. %)			Co:Cu	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Phase composition
	La	Cu	Co			
A_550	-	-	-	-	190	$\gamma\text{-Al}_2\text{O}_3$
LA_550	0.30	-	-	-	172	$\gamma\text{-Al}_2\text{O}_3$
A_1050	-	-	-	-	40	$\theta\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$
LA_1050	0.20	-	-	-	109	$\theta\text{-Al}_2\text{O}_3$
SA_550	-	5.69	4.68	0.82	129	$\gamma\text{-Al}_2\text{O}_3$, Co_3O_4 (CuCo_2O_4)
SLA_550	0.23	4.23	8.05	1.90	138	$\gamma\text{-Al}_2\text{O}_3$, CuCo_2O_4
SA_1050	-	2.74	3.65	1.33	32	$\alpha\text{-Al}_2\text{O}_3$, CuAl_2O_4 and CoAl_2O_4
SLA_1050	0.15	2.52	3.98	1.58	69	$\theta\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, traces of CuAl_2O_4 and CoAl_2O_4

3. RESULTS AND DISCUSSION

The data in Table 1 show that the Cu and Co contents for the La-modified catalyst differ from those obtained for the non-modified catalyst. The Co:Cu weight ratio for the unmodified SA_550 sample (0.82) is lower than that in the (Cu+Co) impregnating solution (1.99). This discrepancy in

the Co:Cu ratios was attributed to the so called “chromatographic effect” of the support [12] and was related to the different affinities of the Al_2O_3 support towards the Cu and Co ions in the impregnating solution. Doping the support with La prevented this effect and the Co:Cu ratio for La-modified catalyst SLA_550 was 1.90, which was close to that in the impregnating solution (1.99).

Therefore, the modification with La is an efficient way to eliminate the selective adsorption of metal ions during impregnation of alumina with nitrate solution, which is important for the multi-component oxide catalyst preparations. The data in Table 1 clearly reveal the stabilization role of La on the specific surface area of the carriers. The surface area of a La-doped catalyst aged at 1050°C (SLA_1050) is twice as higher than that of the corresponding non-doped with La (SA_1050) catalyst. The XRD data on the support (A_550) indicate the presence of $\gamma\text{-Al}_2\text{O}_3$ phase and this pure $\gamma\text{-Al}_2\text{O}_3$, treated at 1050°C (A_1050), is being transformed into $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ phases. The La-modified alumina (LA_1050) did not contain any $\alpha\text{-Al}_2\text{O}_3$ phase, as it can be seen in Table 1. No La-containing phases are observable in the XRD pattern of La-modified samples and the probable

reason for it is the low concentration of the well-dispersed La on the surfaces of the supports [14, 6].

Reflections due to aluminates CuAl_2O_4 and CoAl_2O_4 emerge from the XRD patterns of both non-doped and La-doped Cu-Co catalysts. However, aluminate formation is much less pronounced in the case of the La-modified sample SLA_1050. This implies that the modification with La hampers the interaction of the parent alumina with the active Cu-Co phase. This is in agreement with the findings by Bettman *et al.* [15], who reported that aluminate phases did not form at temperatures lower than 1100°C, when the La_2O_3 content was less than 4 wt.%. The catalytic

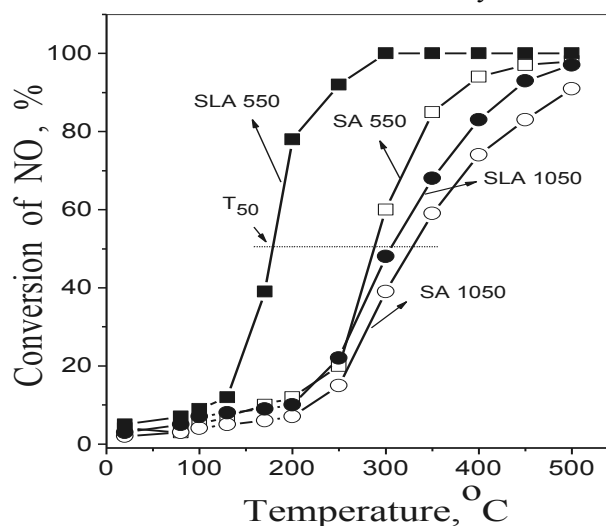


Fig. 1. Temperature dependence of the conversion degree of NO with samples: La-modified - SLA_550 (■) and SLA_1050 (●) and non-modified SA_550 (□) and SA_1050 (○).

reduction of NO by CO and the catalytic oxidation of CO and C₆H₆ by O₂ were carried out on non-modified SA_550 and SA_1050 samples and also on La-modified SLA_550 and SLA_1050 catalysts. The NO conversion – temperature data are presented in Figure 1. The La-modified catalyst has a higher activity in the NO+CO reaction, compared to non-modified catalysts. The temperature T₅₀ for the modified catalyst SLA_550 is by 100°C lower than that measured with the unmodified catalyst SA_550. Modification of the γ -Al₂O₃ support with La has a positive effect on the activity of Cu-Co catalysts in the NO reduction reaction.

Figure 2 presents data from the temperature programmed reaction (TPR) experiments with (NO+CO) gaseous mixture, performed both with the SA_550 and the SLA_550 catalysts. These catalysts have close surface area values and similar XRD patterns. The catalysts were initially treated for 1h at 200°C with the same NO+CO+Ar reaction gas mixture, which has been used for the catalytic activity tests (Fig. 1). Thereafter the catalysts were cooled down to room temperature in an Ar flow and adsorption of NO+CO+Ar gas mixture was carried out at the same temperature for 30 min.

As it is seen in the TPR patterns (Fig. 2) CO, CO₂ and NO are being simultaneously desorbed within a narrow temperature region 50-90°C with both types of catalysts. The TD profiles and the TD_{max} ≈ 60°C for CO desorption from both catalysts is similarly quite close. However, the integrated surface area of the CO TD peak in the case of La-modified sample, SLA_550, is twice as large as that measured with the non-modified catalyst SA_550. The TD pattern of CO₂ for the SLA_550 catalyst has a wide peak with TD_{max} ≈ 125°C, which is not present in the pattern of the SA_550 sample. The TD profile for NO desorption in the case of SLA_550 catalyst is slightly widened towards the lower temperatures. Therefore, on the basis of the (NO+CO)-TPR data it can be concluded that the main difference between the SA_550 and SLA_550 catalysts, is the increased amount of desorbed gases from the latter catalyst. This means that the La-

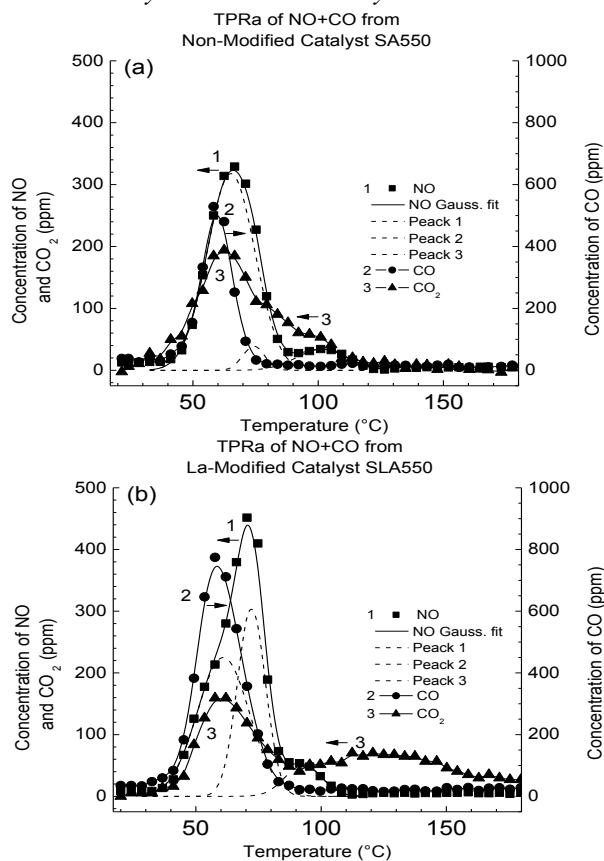


Figure 2. TD patterns of NO, CO and CO₂ obtained after initial adsorption of a NO+CO+Ar gas mixture at 25°C.

modified catalyst has an increased number of active sites for adsorption of NO, CO and CO₂. Both reactants, namely NO and CO, should be adsorbed on the surface of the catalyst for the reaction to occur. As it was discussed above, La ensures Co:Cu ratios for the supported active CuCo-spinel, which are close to that in the stoichiometric CuCo₂O₄ spinel. The presence of bivalent catalytically active sites playing the role of donor-acceptor pairs is a well-established requirement for the activity of oxide catalysts in different redox reactions [6, 16].

The results obtained for the oxidation of CO by molecular O₂ are presented in Fig. 3. The reaction conditions were as follows: 0.5 vol. % CO, 1 vol.% O₂, balance Ar and GHSV 20 000 h⁻¹. Comparison of T₅₀ measured with non-modified

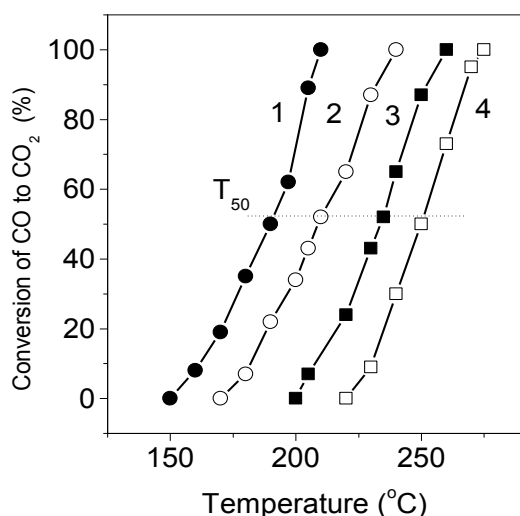


Fig. 3. Comparison of the activity of non-modified and La-modified Cu-Co oxide catalysts in the reaction of catalytic oxidation of CO by O₂. 1-SLA_550, 2-SA_550, 3-SLA_1050, 4-SA_1050.

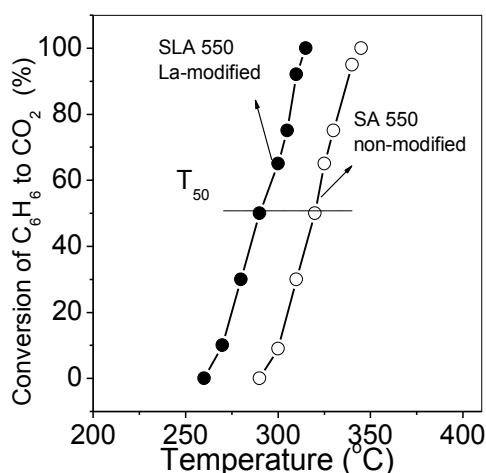


Fig. 4. Comparison of the activity of non-modified and La-modified Cu-Co oxide catalysts in the reaction of complete oxidation of C₆H₆ by O₂.

and La-modified catalysts clearly indicates the beneficial role of La modification for thermal stabilization of the catalytic activity with respect to CO oxidation. A thermal treatment at 1050°C strongly hinders the CO+O₂ reaction on non-modified SA_550 catalyst causing a 50°C shift in T₅₀ towards the higher temperature. In the case of

La-modified catalyst SLA_550, thermal ageing at 1050°C leads to a T₅₀ shift of only 20°C to the higher temperatures. Modification with La improves the catalytic performance of Cu-Co catalysts in the reaction of complete oxidation of C₆H₆ with molecular O₂ as well. The reaction conditions were: 0.04 vol. % C₆H₆, 1 vol. % O₂, ballast Ar and GHSV 20 000 h⁻¹. The promoting effect of La concerns both the activity and the thermal stability of catalysts, as it is seen in Figure 4. The temperature for 50 % conversion of NO in the case of La-modified catalyst SLA_550 is with 30°C lower than T₅₀ measured for the unmodified catalyst SA_550. The role of La-modification of Cu-Co oxide catalysts is to prevent the interaction of the active Cu-Co oxide phase with the alumina support to form aluminates, and as a result of this to preserve the surface area and the number of catalytically active sites. The results of this paper show that the simultaneous presence of Cu, Co and La on the catalyst surface has a synergistic effect with respect to the thermal durability of the Cu-Co oxide catalysts supported on alumina and a positive effect on the NO+CO, CO+O₂ and C₆H₆+O₂ reactions.

4. CONCLUSIONS

The modification of γ-Al₂O₃ support with La at a loading below 3 wt. % has a positive effect on the catalytic performance of supported Cu-Co oxide catalysts. Lanthanum plays a stabilizing role for the specific surface area of carriers and Cu-Co oxide catalysts; the addition of La suppresses the γ→α transformation of the alumina support and its interaction with the active Cu-Co oxide phase to produce aluminates. Modification of the support with La prevents the dissolution of Cu ions into the γ-Al₂O₃ during the impregnation with Cu-Co nitrates. Thus, the active Cu-Co oxide spinel phase supported on La/Al₂O₃ has a higher Co:Cu ratio, which is close to that in the stoichiometric CuCo₂O₄ spinel. The La-modified catalysts have higher activity towards the NO+CO, CO+O₂ and C₆H₆+O₂ reactions, compared to non-modified catalysts. Incorporation of La into the support does not change the energetic status of catalytic active sites but rather increases the number of these sites.

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ВЛИЯНИЕТО НА La ВЪРХУ АКТИВНОСТТА И ТЕРМИЧНАТА СТАБИЛНОСТ НА Cu-Co ОКСИДНИ КАТАЛИЗАТОРИ НАНЕСЕНИ ВЪРХУ НОСИТЕЛ ОТ ДВУАЛУМИНИЕВ ТРИОКСИД

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(Резюме)

В работата са представени Cu-Co оксидни катализатори върху модифициран с La алуминиев носител. Образците са получени по метода на импрегниране от водни разтвори на нитрати съдържащи Cu и Co на носители (γ -Al₂O₃ и модифициран с La Al₂O₃). Образците са охарактеризирани чрез ICP анализ, рентгенофазово и по метода на БЕТ. Реакциите на редукция на NO с CO и окислението на CO и C₆H₆ с O₂ са осъществени върху модифицирани и немодифицирани с La катализатори. Модифицирането на γ -Al₂O₃ с La под 3тегл.% има позитивен ефект върху каталитичните отнасяния на нанесените Cu-Co оксидни катализатори, като добавянето на La потиска образуването на α -Al₂O₃, както и възпрепятства взаимодействието на активната Cu-Co оксидна фаза с носителя и образуването на алуминати. Модифицирането на носителя с La предотвратява внедряването на Cu йони в γ -Al₂O₃ по време на импрегнирането с Cu-Co нитрати. Така активния Cu-Co оксиден шпинел, нанесен върху La/Al₂O₃ има съотношение Co:Cu, което е близо до това на стехиометричния CuCo₂O₄ шпинел. Модифицираните с La катализатори притежават висока активност по отношение на NO+CO, CO+O₂ и C₆H₆+O₂ реакциите, в сравнение с немодифицираните катализатори. Вграждането на La в носителя не променя енергетичната природа на каталитично - активните центрове, а по-скоро увеличава броя на тези центрове.