

# THE PHASE COMPOSITION SPECIFIC SURFACE AND MECHANICAL PROPERTIES OF COMPOSITE MATERIALS

## $R_2O_3$ - $Al_2O_3$ (R = Y, La, or Ce).

E. M. Moroz and A. S. Ivanova

*Borshkov Institute of Catalysis, Siberian Division, Russian Academy of Sciences  
Novosibirsk, 630090 Russia*

**SUMMARY:** Physical and chemical properties of  $R_2O_3 - Al_2O_3$  compounds (R = Y, La, Ce), prepared either by coprecipitation or by mixing the components, are studied. The interaction between the components weakens in the sequence:  $Y_2O_3-Al_2O_3 > La_2O_3 - Al_2O_3 > Ce_2O_3-Al_2O_3$  (no interaction in the last system). All other conditions being the same, the interaction in the precipitated samples exceeds that in the mixed sample. Coprecipitated  $R_2O_3 - Al_2O_3$  samples demonstrate high dispersion and thermal stability; the specific surface area for the mixed samples is somewhat smaller than that for the coprecipitated samples. The pore structure of the samples is determined by the  $R_2O_3$  nature: yttria – alumina and lanthana – alumina samples demonstrate a polydispersed distribution of pore sizes, and narrow micropores are typical of the ceria-alumina system.

**KEYWORDS:** absorption, composite material, aluminum-matrix composites, mechanical strength.

### INTRODUCTION

$R_2O_3 - Al_2O_3$  compounds can be used as both high-temperature supports and catalysts for the total oxidation of hydrocarbons [1]. According to [2], the addition of yttria or lanthana to hydrargillite promotes the formation of  $\alpha-Al_2O_3$ ; however, the addition of cerium oxide retards this process. Other data are reported in [3], where a high-temperature shift by  $\sim 373$  K for the phase transformation  $\gamma-Al_2O_3 \rightarrow \alpha-Al_2O_3$  was detected in the presence of lanthana. Taking into account the discrepancies of these data and the lack of information about the structure and strength of the  $R_2O_3-Al_2O_3$  compounds, the aim of our work is to study the influence of both the synthesis method and the nature and concentration of  $R_2O_3$  (R = Y, La, Ce). In addition, we intend to study the calcination temperature on the phase composition, surface, and the mechanical properties of the aforementioned systems.

## EXPERIMENTAL

Two series of samples differing in the preparation method were studied. The samples of Series I were prepared by coprecipitation with a water-ammonia solution, at pH 9 and 343 K, under intensive stirring. The corresponding mixtures of solutions of aluminum and salts of rare-earth elements (REE) taken in specified proportions were used. Suspensions were aged under the given conditions for 2 h, filtered, and washed by distilled water until the nitrate ions were no longer present. The samples of Series II were prepared by the wet mixing of hydroxides of aluminum and corresponding REE at a given calculated humidity of the slurry. All the samples were air-dried at 293 K and 383 K for 12 h and then calcined for 4 h in an air stream at 673 - 1523 K

The component content in the samples was analyzed according to [4]. An HZG-4C diffractometer was used for the X-ray phase analysis (CuK $\alpha$ -radiation, graphite monochromator). Parameters of elementary cells for corresponding solid solutions were determined within an accuracy of  $\pm 0.003 \text{ \AA}$ . The size of the region of coherent scattering (RCS) was calculated by the Scherrer formula. The specific surface area of the samples was measured using the method of argon thermal desorption [5], and the porosity was determined using an Hg porosimeter (Pore Sizer-9300). The mechanical crushing strength was measured by a MP-9C apparatus for 30 pellets and taken as the average.

## RESULTS AND DISCUSSION

The phase composition of the binary samples for Series I is given in Table 1. The yttria-lanthana-alumina samples, calcined at 673 K, are X-ray amorphous, except for the sample with ~25 mol %  $\text{La}_2\text{O}_3$ , demonstrating the presence of a  $\text{La}_2\text{O}_3$  phase. Cerium-aluminum samples are the mixtures of the dispersed phase ( $\text{RCS} \leq 2 \text{ nm}$ ) and cerium dioxide with RCS not exceeding .5nm.

A rise in the temperature of the thermal treatment to 973 K for the samples containing Y or La ( $\text{R}_2\text{O}_3 \leq 10 \text{ mol } \%$ ), leads to the formation of solid solutions based on  $\gamma\text{-Al}_2\text{O}_3$ . The parameter of the elementary cell for the solid solutions mentioned above increases with a rise in the  $\text{R}_2\text{O}_3$  content within the ranges 7.969 - 8.031  $\text{ \AA}$  and 7.932 - 7.975  $\text{ \AA}$  for Y- and La-containing samples, respectively (Table 1). The formation of these compounds has been noted earlier [6]. The samples  $\text{R}_2\text{O}_3 - \text{Al}_2\text{O}_3$  ( $\text{R} = \text{Y}, \text{La}$ ) with ~25 mol %  $\text{R}_2\text{O}_3$ , retain the same phase composition after calcination at temperatures exceeding 673 K,  $\text{La}_2\text{O}_3$  formed is hydrated readily upon exposure to air (Table 1). The ceria - alumina samples, treated at 973 K, contain two phases,  $\gamma\text{-Al}_2\text{O}_3$ , and  $\text{CeO}_2$ , with their parameters of elementary cells corresponding to standard parameters. No product of interaction between the starting compounds is detected. The RCS values for cerium dioxide virtually do not change, which demonstrates the lack of sintering in the range 673 - 973 K.

Calcination of the samples at 1273 K gives rise to the appearance of a minor amount of lanthanum- or yttrium-containing aluminates with the perovskite ( $\text{RAlO}_3$ ), garnet granate ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) structures, the solid solutions on the basis of  $\gamma\text{-Al}_2\text{O}_3$  being the main component of the samples. The phase composition of ceria-alumina samples remains unchanged, and only a two fold increase of the RCS size is observed (Table 1).

The samples of Series II, calcined at 1273 K, are essentially the mixtures of corresponding oxides, dissimilar to the above-mentioned cases. The parameters of elementary cells coincide well with the standard data (Table 2). Alumina at this calcination temperature is present in the form of  $\gamma$ - $\text{Al}_2\text{O}_3$ . Lanthana – alumina samples with a  $\text{La}_2\text{O}_3$  content exceeding 10 mol % contain the solid solution on the basis of  $\gamma$ - $\text{Al}_2\text{O}_3$ , and lanthanum aluminate,  $\text{LaAlO}_3$ , (resembling the samples of Series I). The unit cell parameter for this solid solution exceeds the one of pure  $\gamma$ - $\text{Al}_2\text{O}_3$ , but the exact value is not given because of a minor contribution of this phase.

A rise in the calcination temperature to 1323 K leads to the appearance of the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase in the samples  $\text{R}_2\text{O}_3 - \text{Al}_2\text{O}_3$  with  $\text{R} = \text{Y}, \text{Ce}$ . Some traces of the solid solution on the basis of  $\gamma$ - $\text{Al}_2\text{O}_3$  are present in the  $\text{La}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  system. At the same time, the formation of a minor admixture of yttrium or lanthanum aluminates,  $\text{YAlO}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and  $\text{LaAlO}_3$  and  $\text{La}_2\text{Al}_{29}\text{O}_{39}$ , takes place in yttria-alumina and lanthana – alumina samples. In accordance with [7], no products of interaction are detected in the ceria – alumina samples of Series II (Table 2).

Thus, the study of the phase composition of the samples (Series I and II) demonstrates the less pronounced interaction between components of the binary systems prepared by mixing, as compared to the coprecipitated samples. Moreover, the interaction decreases in the sequence  $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3 > \text{La}_2\text{O}_3 - \text{Al}_2\text{O}_3 > \text{Ce}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  (the complete lack of the interaction for the last system is caused by structural peculiarities of  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$ ).

The surface area of the binary samples of Series I depends on both the nature of  $\text{R}_2\text{O}_3$  and the temperature of the thermal treatment. Part of the figure shows that the specific surface area of both yttria-alumina and lanthana – alumina samples, containing 5%  $\text{R}_2\text{O}_3$ , reaches the maximum value (exceeding the surface area of pure  $\text{Al}_2\text{O}_3$ ) after calcination at 673 K. The specific surface area of the ceria – alumina sample with the same ratio of components does not noticeably differ from the surface of pure  $\text{Al}_2\text{O}_3$ . For the yttria-alumina and lanthana-alumina samples, a rise in the  $\text{R}_2\text{O}_3$  content is accompanied by a gradual decrease in surface area. For the ceria – alumina samples, the surface area first decreases to some level and then remains constant. The dispersion effect for  $\text{R}_2\text{O}_3 - \text{Al}_2\text{O}_3$  (5 mol %  $\text{R}_2\text{O}_3$ ) with  $\text{R} = \text{Y}$  and  $\text{La}$  is caused by the insertion of these cations, which have larger ionic radii than  $\text{Al}$ , into the structure of the solid solution on the basis of  $\gamma$ - $\text{Al}_2\text{O}_3$ . This effect is absent in the ceria – alumina samples for which no interaction is detected.

A rise in the calcination temperature to 973 K leads to a decrease in the absolute values of the specific surface area, but the relationship between the surface area and the nature of REE (part b of the figure) resembles that mentioned above for 673 K. For the samples of Series I, the influence of the nature of REE becomes negligible only after calcination at 1273 K; for all the samples, the specific surface area first increases to a maximum and then gradually decreases. Yttria – alumina samples demonstrate the highest thermal stability. After calcination at 1273 K, the specific surface areas of binary samples with 5 - 10 mol %  $\text{R}_2\text{O}_3$  (170- 200 m<sup>2</sup>/g) exceed the surface areas of pure  $\text{Al}_2\text{O}_3$  by a factor of 2.

The same type of dependence of the specific surface area on the  $\text{R}_2\text{O}_3$ , nature and content is observed for the samples of Series II, calcined at 1273 - 1523 K [Figs. (d) and (e)]. For the samples calcined at 1523 K, we note only an increase in the thermal stability of the lanthana-alumina system and a decrease in the heat resistance of the ceria – alumina samples [Figure (e)]. This may be caused not only by a change in the phase composition, but also by the transformation of the pore structure, which influences the rate of high-temperature sintering.

Indeed, the binary samples of Series II demonstrate a difference in the pore-size distribution (Table 3). A polydispersed distribution, containing a part of pores with  $r > 100$  nm holding ~30% of the total pore voids  $V_z$ , is typical of yttria – alumina and lanthana – alumina samples. Furthermore, the contribution of narrow pores decreases with an increase in the  $R_2O_3$  content, and the redistribution of meso- and macropores occurs. Narrow micropores are typical of ceria – alumina samples, where no pores with  $r > 100$  nm are detected (Table 3). From the results obtained, we conclude that the reduced thermal stability of ceria – alumina samples is caused by their microporous structure, which promotes sintering.

As a rule, the mechanical strength depends on the presence of macropores [8]. Therefore, as expected, the ceria-alumina samples demonstrate the highest strength (Table 3). The greater the contribution of macropores with  $r > 100$  nm., the lower the strength of yttria – alumina and lanthana – alumina samples. The lanthana – alumina sample with 25 mol %  $La_2O_3$  demonstrates the lowest strength: even after calcination at 1250°C its mechanical crushing strength is only ~10 kg/cm<sup>2</sup>. This is insufficient for use in the synthesis of high-temperature catalysts. We believe that such a sharp drop in mechanical strength can be caused by the easy hydration of lanthana-containing samples in the air. X-ray analysis confirms that the higher the content of lanthana in a binary sample, the more intense the hydration process (Table 1): the reflections typical of  $La(OH)_3$  appear after the contact between the samples and air.

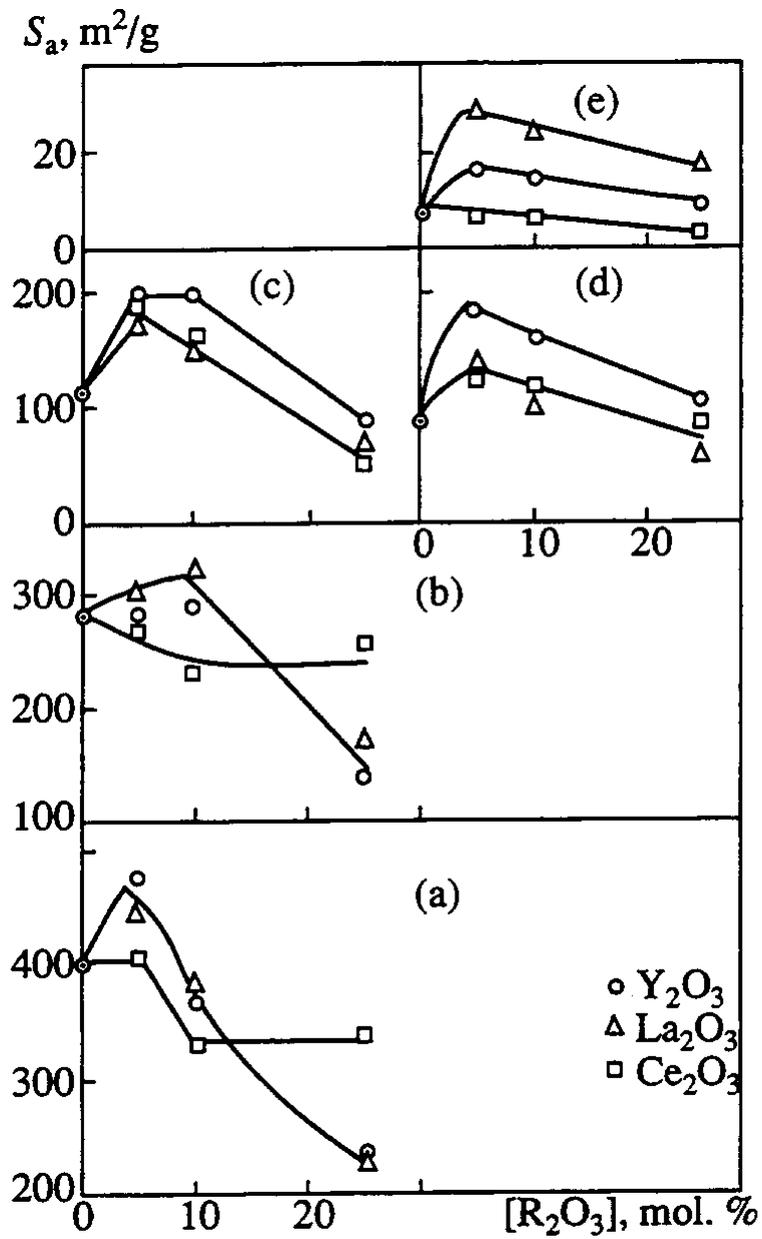
Thus, the study of  $R_2O_3 - Al_2O_3$  compounds ( $R = Y, La, \text{ or } Ce$ ) shows that, owing to their physicochemical and structural properties, these samples can be used as supports for the preparation of high-temperature catalysts, except for those with an insufficient mechanical strength.

On the other hand, these systems are rather effective catalysts for the total oxidation of carbon monoxide. The most suitable for this reaction are the lanthana – alumina samples with 5 – 25mol%  $La_2O_3$ . The temperature that is necessary to attain a 25% conversion of CO in these samples is lower than that for pure  $Al_2O_3$ , (Table 4). In addition, the specific surface area of the binary samples is smaller than that of  $Al_2O_3$  by a factor of 2- 4 (Table 4).

## REFERENCES

1. Kilbourn, B.T., *J. Less-Common Met.*, 1986, vol. 126, p. 101.
2. Vereshchagin, V.I., Zelinskii, V.Yu., Khabas, G.A., and Kolova, I.I., *Zh. Prikl. Khim.*, 1982, vol. 55, no 9, p. 1946.
3. Shaper, H., Doesburg, E.B., and van Reijen, L.L., *Appl. Catal.*, 1983, vol. 7, no. 2, p. 211.
4. Price, W., *Analytical Atomic Absorption Spectroscopy*, New York: Wiley, 1972.
5. Buyanova, N.E., Karnaukhov, A.P., and Alabuzhev, Yu.A., *Opredelenie Poverkhnosti Dispersnykh i Poristykh Materialov* (Measurement of the Surface Area for Dispersed and Porous Materials), Novosibirsk: Inst. of Catalysis, Siberian Division of the Russian Academy of Sciences, 1978.
6. Mizuno, M. and Yamada, T., *Rep. Gov. Ind. Res. Inst.*, vol. 39, no. 4, p. 157.
7. Osama, M. and Kimura, M., *J. Mater. Sci. Lett.*, 1990, vol. 9, no 3, p. 291.
8. Dzis'ko, V.A., Tarasova, D.V., and Karnaukhov, A.P., *Fiziko-Khimicheskie Osnovy Sinteza Okisnykh Kataliza-torov* (Physicochemical Bases for Synthesis of Oxide Catalysts), Novosibirsk: Nauka Sib. Otd., 1978, p. 296.

Figure 1



The relation between the  $R_2O_3$  content and the specific surface area of (a) - (c) coprecipitated and (d) and (e) mixed binary  $R_2O_3 - Al_2O_3$  samples ( $R = Y, La, Ce$ ) calcined at temperatures: (a) 673, (b) 973, (c, d) 1273, and (e) 1523 K.

Table 1. Phase composition of coprecipitated R<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> compounds (R = Y, La, Ce)

System	R <sub>2</sub> O <sub>3</sub> Content, mol %	Phase composition											
		673 K			973 K				1273 K				
		Al <sub>2</sub> O <sub>3</sub>		R <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>		R <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>		R <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	R <sub>2</sub> O <sub>3</sub>	
		phase	phase	RCS,A	phase	a,A	phase	RCS,A	phase	a,A	phase	phase	RCS,A
Y-AL-O	4.9	X-ray amorphous		-	γ	7.969	-	-	γ	7.922	-	-	
	10	X-ray amorphous		-	γ	8.031	-	-	γ	7.943	YAlO <sub>3</sub> , Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	-	
	24.8	X-ray amorphous		-	X-ray amorphous				γ	traces*	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	-	
La-Al-O	4.8	X-ray amorphous		-	γ	7.932	-	-	γ	7.932	-	-	
	9.5	X-ray amorphous		-	γ	7.975	-	-	γ	7.922	LaAlO <sub>3</sub>	-	
Ce-Al-O	25	-	La <sub>2</sub> O <sub>3</sub>	-	γ	-	La <sub>2</sub> O <sub>3</sub>	-	γ	traces	LaAlO <sub>3</sub> , La(OH) <sub>3</sub> traces	La <sub>2</sub> O <sub>3</sub>	
	4.5	HDC**	CeO <sub>2</sub>	50	γ	7.912	CeO <sub>2</sub>	50	γ	7.907	-	CeO <sub>2</sub>	
	9.9	HDC	CeO <sub>2</sub>	45	γ	7.911	CeO <sub>2</sub>	50	γ	7.911	-	CeO <sub>2</sub>	
	23.5	HDC	CeO <sub>2</sub>	50	γ	7.911	CeO <sub>2</sub>	50	γ	7.911	-	CeO <sub>2</sub>	

Notes: \*Traces (3 = 5 %).

\*\*Highly dispersed compound with RCS << 2 nm; the parameter of the CeO<sub>2</sub> elementary cell is equal to 5.411 Å

Table 2. Phase composition of mixed R<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> compounds (R = Y, La, Ce)

System	R <sub>2</sub> O <sub>3</sub> content, mol %	Phase composition									
		1273 K						1523 K			
		Al <sub>2</sub> O <sub>3</sub>			RAIO <sub>3</sub>		R <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	R <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	R <sub>2</sub> O <sub>3</sub>
		phase	phase	RCS,A	phase	RCS,A	phase	RCS,A	phase	phase	phase
Y-AL-O	5	γ	7.880	40	-	-	Y <sub>2</sub> O <sub>3</sub>	500	δ,α	YAlO <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>
	10	γ	7.880	40	-	-	Y <sub>2</sub> O <sub>3</sub>	600	δ,α	YAlO <sub>3</sub> , Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	Y <sub>2</sub> O <sub>3</sub>
	25	γ	7.880	50	-	-	Y <sub>2</sub> O <sub>3</sub>	500	α	YAlO <sub>3</sub> , Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	Y <sub>2</sub> O <sub>3</sub>
La-Al-O	5	not measured			-	-	-	-	Traces**γ	LaAlO <sub>3</sub> , La <sub>2</sub> Al <sub>24</sub> O <sub>39</sub>	-
	10	γ*	-	-	LaAlO <sub>3</sub>	350	-	-	Traces**γ	LaAlO <sub>3</sub>	-
Ce-Al-O	25	γ*	-	-	LaAlO <sub>3</sub>	350	-	-	-	LaAlO <sub>3</sub>	-
	5	γ	7.880	45	-	-	CeO <sub>2</sub>	400	α	-	CeO <sub>2</sub>
	10	γ	7.880	40	-	-	CeO <sub>2</sub>	400	α	--	CeO <sub>2</sub>
	25	γ	7.880	50	-	-	CeO <sub>2</sub>	500	α	-	CeO <sub>2</sub>

Note: \* Solid solution on the basis of γ-Al<sub>2</sub>O<sub>3</sub>.

\*\* Traces (3 - 5%).

Table 3. Textural parameters of mixed R<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> compounds (R = Y, La, Ce)

System	R <sub>2</sub> O <sub>3</sub> content, mol %	1273 K						1523 K					
		V <sub>Σ</sub> <sup>3</sup> /g	Pore size distribution, cm <sup>3</sup> /g				Strength, kg/cm <sup>2</sup>	V <sub>Σ</sub> <sup>3</sup> /g	Pore size distribution, cm <sup>3</sup> /g				Strength, kg/cm <sup>2</sup>
			1.5-10nm	10-100nm	100-1000nm	>1000 nm			1.5-10 nm	10-100 nm	100-1000 nm	>1000 nm	
Y-AL-O	5	0.73	0.44	0.07	0.18	0.04	65	0.28	0	0.12	0.12	0.04	100
	10	0.71	0.38	0.08	0.19	0.06	60	0.32	0.01	0.16	0.14	0.01	80
	25	0.74	0.35	0.11	0.20	0.08	60	0.31	0.01	0.13	0.13	0.04	80
La-Al-O	5	0.51	0.36	0	0.08	0.07	70	0.41	0	0.30	0.09	0.02	80
	10	0.60	0.35	0.01	0.20	0.04	50	0.46	0.02	0.22	0.17	0.05	60
	25	0.61	0.27	0.04	0.15	0.15	8	0.48	0.02	0.10	0.24	0.12	10
Ce-Al-O	5	0.45	0.43	0.02	0	0	100	0.32	0	0.32	0	0	200
	10	0.33	0.25	0.08	0	0	90	0.25	0.06	0.19	0	0	220
	25	0.30	0.16	0.10	0.04	0	90	0.20	0	0.16	0.04	0	240

Table 4. Influence of the nature of the system on its activity in carbon monoxide oxidation\*

System	La <sub>2</sub> O <sub>3</sub> content, mol %	Calcination temperature, K	S <sub>spec.</sub> , m <sup>2</sup> /g	Temperature necessary to attain a 25 % CO conversion, K
La <sub>2</sub> O <sub>3</sub> - Al <sub>2</sub> O <sub>3</sub>	5	1273	140	503
	10	1273	100	473
	25	1273	60	498
Al <sub>2</sub> O <sub>3</sub>	0	823	280	518

\*Activity of the samples was estimated by the temperature necessary to attain a 25% CO conversion under standard conditions: the gas flow rate 1 l min<sup>-1</sup> cm<sup>-2</sup>, CO content 14 mg/l, catalyst bed depth 5 cm. Accuracy of measurement+5%.