

RKCL2971

## MO-ZrO<sub>2</sub> CATALYSTS FOR NITROGEN OXIDES REDUCTION BY HYDROCARBONS IN OXYGEN EXCESS. PREPARATION AND PROPERTIES

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*Received January 12, 1996*

*Accepted March 11, 1996*

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### Abstract

The physico-chemical and catalytic properties of MO-ZrO<sub>2</sub> systems (where M is Ca, Sr, Ba) have been studied as a function of the synthesis parameters. Finely powdered heterogeneous mixtures of solid solutions with cubic+monoclinic or tetragonal+monoclinic phase composition were found to be formed. These systems possess quite good high-temperature activity in the reaction of NO<sub>x</sub> selective reduction by propane under oxygen excess. For a given system, the rate constant depends linearly upon the M-O bond dissociation energy in the surface layer, the slope being positive for Ca and Sr and negative for Ba.

*Keywords:* Modified zirconias, catalysts, preparation, properties, nitrogen oxides reduction

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## INTRODUCTION

Zirconia-based systems are now widely used as catalysts and supports for various processes [1]. To a great extent, this is due to the variety of existing zirconia modifications [2]. Among them, the most interesting for catalysis are the low-temperature phases, whose stability usually depends on the presence of some substituting cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Y<sup>3+</sup>, Sc<sup>3+</sup>, etc.) or anions [3].

The present work aims at studying the effect of the nature and content of alkaline-earth cations as well as synthesis procedure and temperature of

annealing on the physico-chemical and catalytic properties of modified zirconias, the latter being tested in the reaction of NO<sub>x</sub> selective reduction by propane in excess oxygen.

## EXPERIMENTAL

Modified zirconias were obtained either *via* coprecipitation from solutions of the corresponding salts by adding base solutions at constant pH and temperature with subsequent washing and filtering, or by mixing the corresponding components (hydroxides, *etc.*) at a certain humidity of the moulded paste [4]. All the samples were moulded, dried at 383 K for 12 h and calcined at 973-1173 K.

The samples were analyzed for the content of basic components by atomic absorption spectroscopy [5]. X-Ray phase analysis was carried out by means of a URD-6 diffractometer using Cu K<sub>α</sub> radiation. The lattice cell parameters of the solid solution were estimated with an accuracy of  $\pm 0.002 \text{ \AA}$ .

Surface state of the samples was studied by SIMS using an MS-7201 mass-spectrometer. Mass scanning and data processing were performed through KAMAK interface with PC DVK-3. An argon ion beam with an energy of 4 keV and current density of  $20 \mu\text{A}/\text{cm}^2$  was used. Residual pressure in the mass-spectrometer chamber was lower than  $3 \times 10^{-6} \text{ Pa}$  thus ensuring a dynamically pure state of the surface during measurements. The particles of powdered samples were slightly rubbed into a high-purity indium foil without any further pretreatment.

The surface area of the samples was measured by means of argon thermal desorption [6].

The catalytic properties of samples were tested in selective nitrogen oxide reduction by propane under oxidizing conditions. Catalytic activity expressed as a first-order rate constant was estimated from the degree of nitrogen oxide conversion into molecular nitrogen in an integral plug-flow reactor fed by the reaction mixture with a standard initial composition (1000 ppm NO, 1300 ppm C<sub>3</sub>H<sub>8</sub>, 1 vol.% O<sub>2</sub>, balance He) at GHSV equal to  $4000 \text{ h}^{-1}$ . Propane conversion to CO or CO<sub>2</sub> was also estimated.

## RESULTS AND DISCUSSION

According to X-Ray data (Table 1), modified samples calcined at 973 K are composed of a mixture of zirconia modifications, whose structure and relative amount are determined by the nature and concentration of the second

component. For dilute samples, a mixture of the tetragonal and monoclinic phases forms, a higher content of the former being found for the Sr- and Ca-modified systems. As the MO content increases, all samples were transformed either into the mixture of cubic and monoclinic ZrO<sub>2</sub> or cubic ZrO<sub>2</sub>. At higher temperature of calcination (1173K), cubic zirconia is mainly formed.

**Table 1**

Effect of MO nature on the phase composition and surface area of binary samples  
MO-ZrO<sub>2</sub> ( M = Ca, Sr, Ba )

Sample No	MO		Calcination temperature (K)	Specific surface (m <sup>2</sup> /g)	Phase composition <sup>g</sup> 130 a	Phase ratio	D <sup>b</sup>
	Nature	Content (mol %)					
1	CaO	1.5	973	50	T+M	3:1	1.85
2		5.0		85	C+M <sup>c</sup>		1.44
3		10.0		110	C a=5.113		1.40
4	SrO	25.0	973	90	C; a=5.128	2:1	1.37
5		2.0		80	T+M		1.50
6		5.0		90	C+M		1.42
7		10.0		100	C+M <sup>c</sup>		1.33
8		5.0		1173	28		C; a=5.111
9	BaO	5.0	973	100	T+M	2:1	1.70
10		10.0		85	T+M <sup>c</sup>		1.90
11		25.0		87	C+M <sup>c</sup>		1.30
12	ZrO <sub>2</sub>		693	180	T; a=5.099 c=5.162		1.83
13			973	2	M; a=5.151 b=5.217 c=5.327 β=99°26'		

<sup>a</sup> C-cubic ; T- tetragonal; M- monoclinic phases, respectively.

<sup>b</sup> degree of the tetragonal distortion of cubic phase defined in the text.

<sup>c</sup> the relative phase amount is less than 5%

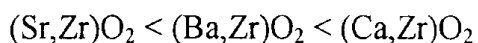
The low-temperature tetragonal and cubic modifications obtained here appear to be solid solutions hosting appropriate cations (for pure zirconia, at 973 K only a monoclinic phase has been detected (Table 1), which agrees well with the

earlier data of Ivanova *et al.* [7]). To prove unambiguously formation of the solid solution, usually estimation of the cell parameters is required. Unfortunately, for heterophase samples reliable determination of zirconia unit cell parameters was found to be impossible due to overlapping of reflections corresponding to various modifications. However, for monophasic samples of cubic zirconia modified by Sr or Ca such estimations have been carried out evidencing formation of solid solutions [8].

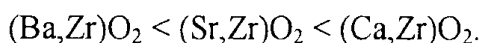
To characterize the degree of tetragonal distortion of the cubic lattice, parameter  $D$  was used, defined as the ratio of halfwidth ( $H$ ) of the diffraction peaks observed in the  $2\theta$  angles range of *ca.*  $50^\circ$  (where reflections 220+022 of the tetragonal and 220 of the cubic phase are located) and those situated at *ca.*  $30^\circ$  (111 reflection for both modifications). For an ideal cubic phase, this parameter is less than 1.4, being determined by a pure instrumental angle-dependent broadening of the diffraction peaks. Based on this estimate, phases with  $D$  values less than 1.4 revealed in heterogeneous and/or homogeneous systems were assigned to a cubic (pseudocubic) space group (Table 1).

The low-temperature modified zirconias of tetragonal and cubic symmetry were found to possess high sintering resistance. Thus, for samples calcined at 973 K surface area of the binary systems significantly exceeds that of pure zirconia (Table 1).

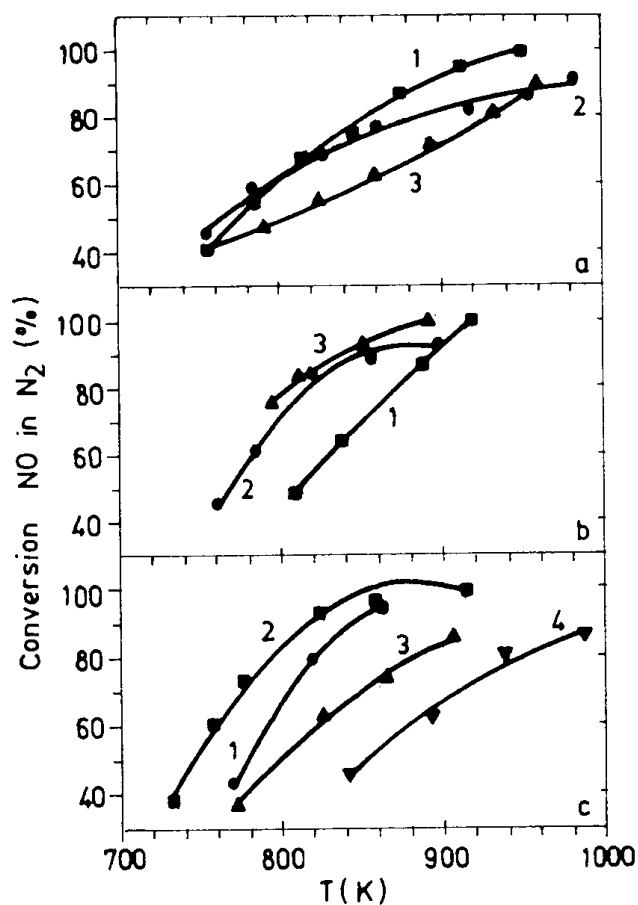
Figure 1 presents temperature dependences of  $\text{NO}_x$  conversion into molecular nitrogen in the oxidizing reaction mixture. As follows from these data, a specific feature of the catalytic properties of modified zirconias is a monotonous increase of  $\text{NO}_x$  conversion with temperature, while for known catalysts [9,10] it usually goes through a maximum. As a result, for the moderate GHSV used here, in high-temperature region high conversions approaching 100% were obtained. For practical purposes, temperatures of the given degree of conversion at constant GHSV are used to characterize relative catalytic activity. For modified zirconias, temperatures of high (90-100%) conversion were found to depend upon the nature of the alkaline-earth cation and its content. Thus, for systems containing 5 mol % MO these temperatures change as follows:



while for 10 mol % MO the sequence is somewhat different:



To characterize catalytic activity more precisely, first-order rate constants normalized to unit surface were calculated; the results for 823 K are given in Table 2. As follows from these data, specific activity is not a simple function of



**Fig. 1.** Temperature dependence of nitrogen oxide conversion for zirconium-containing catalysts calcined at 973 K:  
 a) Ca-Zr-O: 1- 5; 2- 10; 3- 25 mol % CaO;  
 b) Ba-Zr-O: 1- 5; 2- 10; 3-25 mol % BaO;  
 c) Sr-Zr-O: 1- 2; 2- 5; 3- 10 mol % SrO; 4- 5 mol % SrO calcined at 1173 K

Hence, catalytic properties of modified zirconias appear to be determined both by the nature of promoter and by the zirconium dioxide structure. When isomorphous  $M^{2+}$  substitution for  $Zr^{4+}$  occurs, oxygen is removed from the lattice generating anion vacancies and thus changing coordination numbers [11]. To describe more adequately the disordered, partially stabilized zirconias with

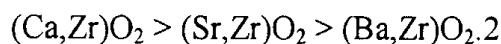
lattice generating anion vacancies and thus changing coordination numbers [11]. To describe more adequately the disordered, partially stabilized zirconias with

**Table 2**  
First-order rate constants for NO<sub>x</sub> selective on modified zirconias  
calcined at 973 K

System	Ca-Zr-O			Sr-Zr-O			Ba-Zr-O		
MO content (mol %)	5	10	25	2	5	10	5	10	25
$k \times 10^2$ (s <sup>-1</sup> m <sup>-2</sup> )	0.85	0.58	0.29	1.73	4.47	0.48	0.36	1.44	1.88
						1.17*			

\* - sample calcined at 1173 K.

fluorite-type structure, usually the distribution of polyhedra typical for a given cation and associated with the disorder of oxygen vacancies is considered. Random distribution is thought to stabilize the more strained symmetric (cubic) form possessing also a higher dispersity. Two factors seem to explain the simultaneous presence of another (monoclinic) phase in some samples, namely, the restricted solubility of cations introduced (thermodynamic factor) and/or the incomplete interaction of components (kinetic factor, which is important for high temperatures of calcination). The first factor mainly depends upon the ionic radii of Me<sup>2+</sup>: the smaller is the ionic radius ( $r_{Zr^{4+}} = 0.82 \text{ \AA}$ ,  $r_{Ca^{2+}} = 1.04 \text{ \AA}$ ,  $r_{Sr^{2+}} = 1.20 \text{ \AA}$ ,  $r_{Ba^{2+}} = 1.38 \text{ \AA}$ ), the larger is the solubility. Indeed, for systems containing 5 mol % MO, relative amount of the cubic phase decreases in the following order:



More subtle details of the effect of substituting cation radius on the zirconia structure can be understood taking into account that the cubic fluorite-type lattice is stable at  $r_k/r_a > 0.732$  [12], while for pure ZrO<sub>2</sub> this ratio is 0.66. So increase of the radius of a guest cation makes smaller the deviation of the host lattice from cubic symmetry (Table 1). At the same time, relaxation of the interatomic distances is expected to increase the M-O bond length for more bulky substituting cations, thus decreasing its strength. Indeed, such a trend in relative M-O bond energies (Ca-O > Sr-O > Ba-O) was revealed by SIMS (*vide infra*).

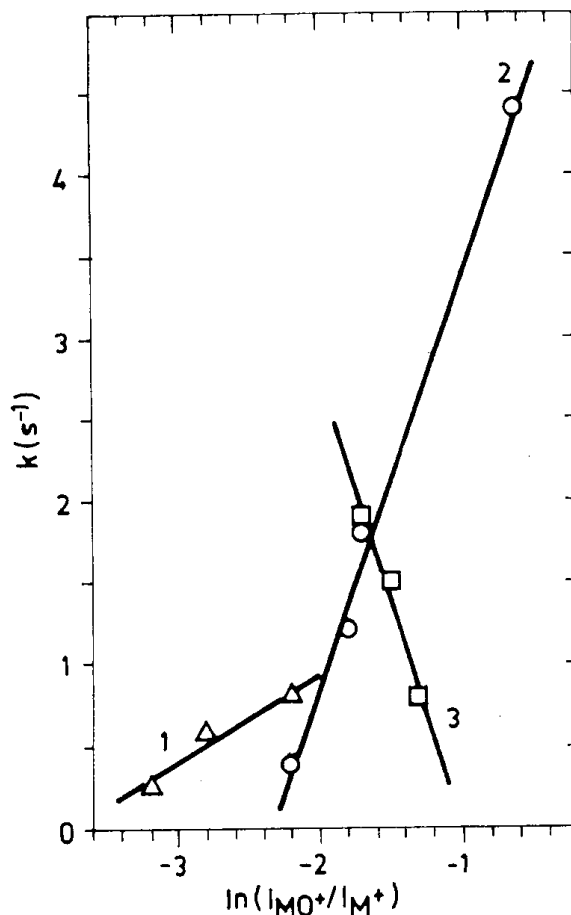


Fig. 2. Reaction rate constants for selective nitrogen oxide reduction *versus* logarithm of the ion current ratio  $I(\text{MO}^+)/I(\text{M}^+)$ :  
 1-calcium-zirconium samples; 2-strontium-zirconium samples; 3-barium-zirconium samples

Figure 2 shows the reaction rate constant versus the logarithm of the ion current ratio  $I(\text{MO}^+)/I(\text{M}^+)$  for the topmost surface layers. According to Wittmaack [13], the latter value is proportional to the M-O dissociation energy. It suggests that the rate constant for selective  $\text{NO}_x$  reduction depend linearly upon the M-O bond strength, the slope being positive for calcium- and strontium-modified samples and negative for the barium-containing systems. To understand these phenomena, the reaction mechanism should be taken into account. Although there is still great controversy in this subject, some tentative

explanation could nevertheless be supposed. First of all, among several types of surface complexes formed by NO adsorption on oxides, the most strongly bound are nitrites and nitrates [14]. At high operating temperatures this is the case for selective NO<sub>x</sub> reduction on modified zirconias, only such strongly bound forms can remain on the surface competing with molecular oxygen for activated hydrocarbons. Recently, *in situ* IR-spectroscopic experiments have shown nitrite-nitrates to be true intermediates in this reaction [15]. In general, the strength of the N-O bond in these complexes is expected to depend essentially on the strength of oxygen bonding with the surface active centers, coordinatively unsaturated zirconium cations. Further, these centers emerge due to surface anion vacancies generated by incorporation of guest cations. Hence, some dependence of the bonding strength of surface oxygen upon the energy of M<sup>2+</sup> - O bond might be supposed. From that point of view, correlation observed implies that the rate-limiting step of the overall reaction includes cleavage of the N-O bond in nitrite-nitrate complexes in the course of their transformation into the product molecular nitrogen.

Though the high sensitivity of SIMS method to fine details of the surface oxygen spectrum might seem rather unexpected, note that a strong dependence of the molecular ion yield on the surface structure is a rather well known phenomenon [16,17]. Another example of this kind is the fact that SrO<sup>+</sup> emission from the sample containing 5 mol % SrO and calcined at 973 K is higher than that from the same sample calcined at 1173 K (Fig. 2). Probably, the cubic solid solution formed at 973 K has a more strained structure that affects M-O bonding strength.

Elevation of the sample calcination temperature to 1173 K was found to decrease their performance in NO<sub>x</sub> reduction mainly due to a fall of the surface area (Fig. 1). To enlarge the surface area for high-temperature samples, a certain amount of alumina was introduced thus stabilizing their activity.

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