mechanism. Temptation to assign a fundamental role to uranium is high but care must be taken not to forget the rich properties of aluminium.

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C8

Effect of Grinding and of the Preparation Method on the Catalytic Activity of Yb_2O_3 Toward Alcohol Decomposition

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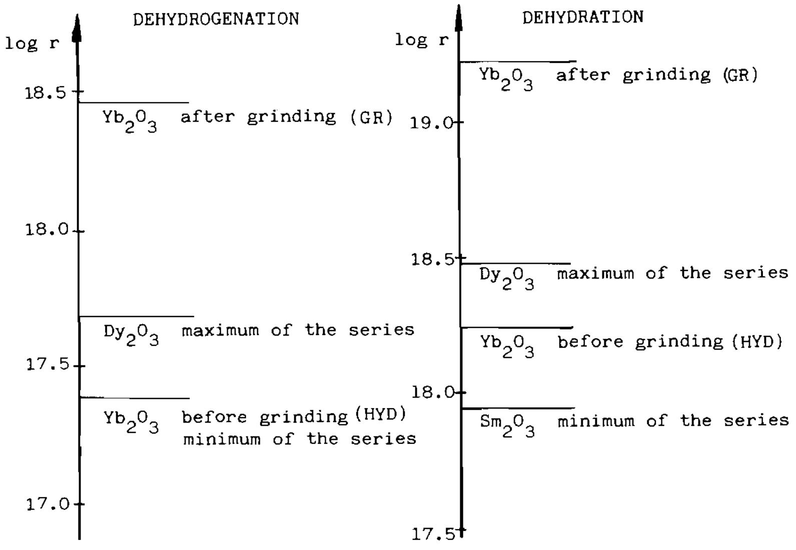
In recent papers it is considered that the catalytic behavior of the lanthanide oxides is closely related to the properties of Ln^{3+} ions [1, 2]. In particular, for alcohol decomposition reactions, a regular variation of activity from La_2O_3 to Lu_2O_3, parallel to the ionic radius of Ln^{3+} is proposed both for dehydration and for dehydrogenation processes [1, 3]. Our results are not in accordance with these ideas [4, 5]. Other aspects like those related to the textural properties of the oxides play an important role, having a significant influence on both the activity and product distribution data. This point is discussed in the present paper.

The catalytic activity has been measured for a series of six lanthanide sesquioxides, La, Sm, Eu, Dy, Ho and Yb, and for CeO_2. All these oxides have been prepared, according to [6], by calcination of the corresponding hydroxide phase. The BET surface area of Yb_2O_3(HYD), 54 m^2 g^{-1}, changes to 5.5 m^2 g^{-1} after a grinding process (sample GR). By calcination of ytterbium oxalate an Yb_2O_3, (OXA), with 24 m^2 g^{-1} was obtained. A commercial MERCK AR sample, (COM), with BET surface of 8.5 m^2 g^{-1} is also considered.

The decomposition of 2-propanol and 2-pentanol was studied in a differential flow reactor at normal pressure. Some additional details are given in [5].

Results and Discussion

According to Fig. 1 the specific activity of Yb_2O_3-(GR) is about 12 times higher than that existing among the series of Ln_2O_3. The difference of activity between both Yb_2O_3 samples does not depend on the temperature (experimental range 600–750 K) and therefore grinding does not cause differences in the selectivity (% dehydration).



r: Activity in molecules m^{-2} s^{-1}

Fig. 1. Catalytic decomposition of 2-propanol. Maximum and minimum values of activity, at 685 K, for the series of La, Sm, Eu, Dy, Ho and Yb sesquioxides. Data corresponding to Yb_2O_3, before and after grinding, are included for comparative purposes.

TABLE I. Product Distribution Data for 2-Pentanol Decomposition, at 698 K, over Different Yb_2O_3 Samples. The limit values for the series of sesquioxides are included.

	% Dehydration	% 1-Pentene	Cis/Trans
Yb_2O_3 (Hydroxide)	86	84	1.7
Yb_2O_3 (Oxalate)	88	94	0.6
Yb_2O_3 (Commercial)	86	89	1.2
Minimum	72 (La_2O_3)	78 (Sm_2O_3)	0.7 (Ho_2O_3)
Maximum	87 (Ho_2O_3)	94 (Ho_2O_3)	1.7 (Sm_2O_3)

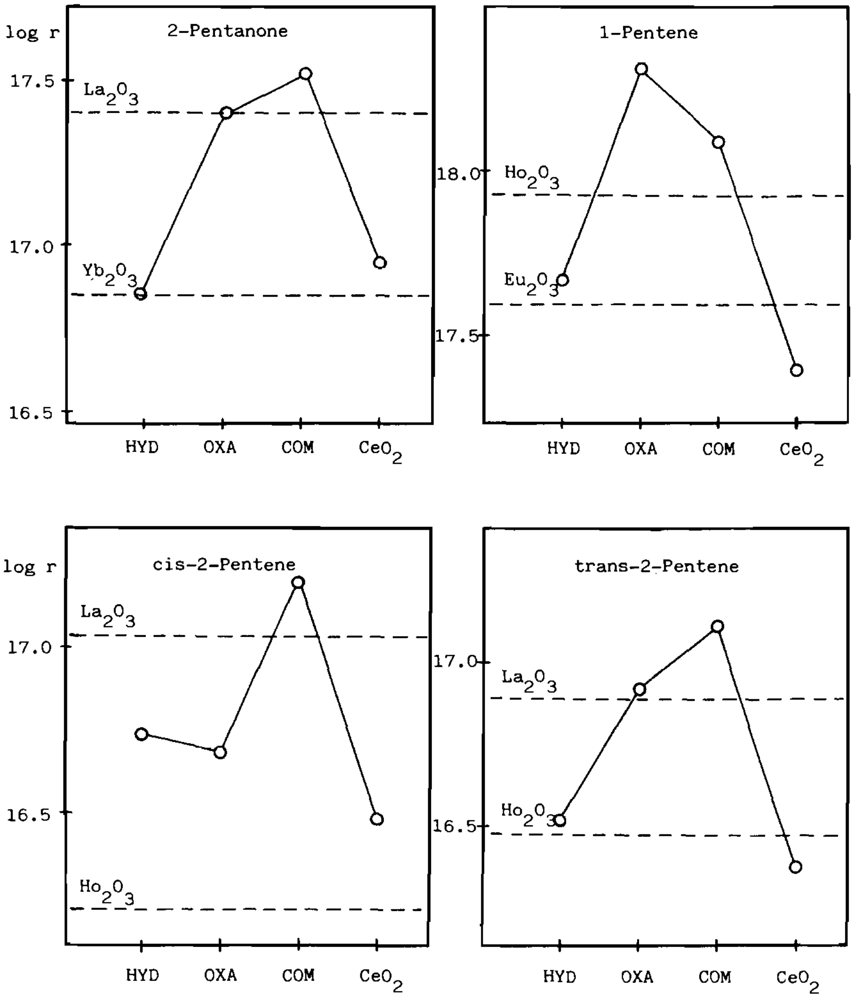


Fig. 2. Activity data in molecules m^{-2} s^{-1}, at 685 K, for 2-pentanol decomposition over three Yb_2O_3 samples: from hydroxide calcination (HYD), from oxalate calcination (OXA) and commercial sample (COM). The values of activity for CeO_2 are also included. Dotted lines indicate the maximum and minimum activity values for the series of six lanthanide sesquioxides prepared by hydroxide calcination (La, Sm, Eu, Dy, Ho and Yb).

For 2-pentanol decomposition, Fig. 2, the influence of the preparation method on the activity of Yb_2O_3 samples is rather similar or even greater than that observed throughout the series of sesquioxides. This is so even in the case of considering the activity data for CeO_2, an oxide with quite different general properties from those of Ln_2O_3. With regard to selectivity data (Table I) for dehydrogenation–

dehydration, as in the case of 2-propanol, no differences are observed among the ytterbia samples. On the contrary, for % 1-pentene and cis/trans ratios the variations are rather analogous to those observed for the sesquioxides.

The study of the textural properties of Yb_2O_3-(HYD) and Yb_2O_3 (GR) shows notable differences to each other, the latter one being an essentially nonporous sample. This suggests that the fraction of the total surface area corresponding to the narrower pores has a minor contribution to the overall reaction rate, which would be more closely related to the external surface area than to BET surface. When Fig. 2 is analysed, it can be deduced that the preparation method affects not only the effective surface area but also, as % 1-pentene and cis/trans ratio changes show, the distribution of centers participating in the dehydration reactions.

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C9

Neodymium Catalysts for Diolefin Polymerization. Influence of the Anionic Ligand Bonded to Neodymium on the Stereospecificity

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Heterogeneous Neodymium containing systems for the polymerization of diolefins to *cis*-1,4 polymers are well known. We have focused our attention on homogeneous catalysts prepared from Neodymium complexes and Aluminum tri-alkyls able to polymerize diolefins and have found that the stereospecificity of the catalysts can be modulated through the variation of several parameters such as the nature of the anionic ligand bonded to Neodymium, the Al/Nd ratio, the concentration and type of Aluminum alkyl in the catalyst. Among these parameters the most efficient in affecting the polymer microstructure is the nature of the anionic ligand bonded to Neodymium. In order to study this effect, the following Nd compounds have been used in combination with $Al(iBu)_3$ for the preparation of the catalysts: $NdCl(OCOCF_3)_2$, $NdCl(OR)_2$, $Nd(OCOCF_3)_3$, $Nd(acac)_3$, $Nd(OR)_3$ (R = isopropyl, neopentyl).

All these catalysts gave polybutadienes with a predominantly 1,4 structure (the content of 1,2 units ranged from 3 to 12%) but with strikingly different *cis/trans* ratios, varying almost continuously from 98.5% *cis*-1,4 with $NdCl(OCOCF_3)_2$ up to 95% *trans*-1,4 with $Nd(OR)_3$ (R = neopentyl).

The nature of the anionic ligand was found to remarkably affect also the rate of polymerization: the halogen containing Neodymium compounds gave the catalysts with the highest activity.