Papers

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Neodimium Catalyzed Diolefin Polymerization

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After about thirty years since the Ziegler-Natta discoveries, the multifaceted aspects of stereospecific catalysis have been hardly clarified, notwithstanding the large amount of research devoted to this subject.

In the same time, extremely active catalysts and simplified processes have been pointed out, particularly in the field of monoolefins. As far as conjugated diolefins are concerned, U [1] and Nd [2] based catalysts have been developed in the last years, besides to more conventional systems based on Ti, V, Co and Ni.

A general characteristic of the quoted catalyst systems is the remarkable amount of alkyl–Al as cocatalyst, required for achieving the best behaviour. Therefore an insight on the reasons of such a large stoichiometric excess is both of theoretical and economical relevance. The possibility of obtaining catalytic complexes with Al/Co = 2 for instance, was early described [3].

Nd catalyst behaves similarly to other systems but shows unusual peculiarities such as: low chain transfer activity with diolefin monomer as well as with monoolefins (ethylene, propene, 1-butene), hydrogen and Et_2Zn; very high sensitivity to cyclopentadiene; low sensitivity to CO; poisoning with alkyl–Mg and $NaAlEt_2H_2$; partial deactivation with hydrocarbons; capability of homo and copolymerizing both butadiene and isoprene to high *cis* polymers, surprising thermal stability. A Nd catalyst is composed of: i) Nd compound, halogen containing or not, able to react with; ii) alkyl–Al unhalogenated compound and iii) metallic halide or organic halogen-derivative, when halogen is absent in i).

The halogen function can be partially displayed by water. By carrying out the catalyst preparation from different Nd and Al compounds and from different halogen donors in hexane and/ or in THF solution, variously active mixtures are obtained. In some cases complexes containing Nd, Al, Cl and alkyl groups in simple ratios to each other can be isolated which are able to polymerize butadiene.

The activity of the above mentioned complexes changes with composition and in some cases is comparable with that of the corresponding homogeneous system in which Al/Nd ratio is extremely higher.

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Catalytic Effect of Uranium Compounds on Alkene Hydrogenation

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The reagent (UCl_3LiAlH_4) was shown [1] to reduce both aromatic and non-aromatic alkenes, among them terpenes.

Among the very surprising results, there is evidence that the closeness of the uranium catalytic cycle depends on the alkene. Some alkenes are fully hydrogenated into the corresponding alkane during the reaction without hydrolysis, for example ethene, propene. Others are found to be partly deuteriated after hydrolysis with deuterium oxide, for example diphenyl-1,1-ethene. In both these cases, the catalytic uranium center is regenerated and less than 10% of uranium per equivalent of alkene is needed. In the other cases, the reduction proceeds, but an intermediate uranium complex (which has not yet been isolated) accumulates and stops the reaction. Thus the full alkene reduction consumes one equivalent of uranium.

It is a contribution to uranium organometallic chemistry as well as to recently developped hydride [3] chemistry. The species 'UCl_2H' formulated by Evans [2] seems to be a possible intermediate in our 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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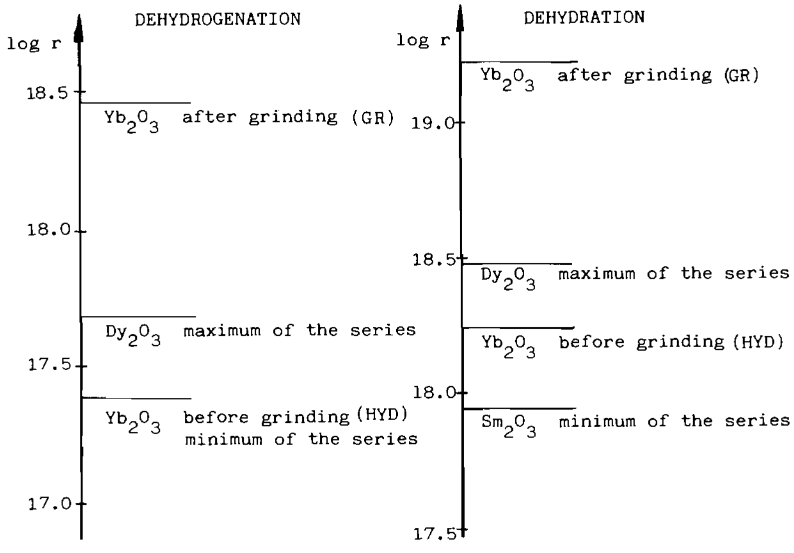
In recent papers it is considered that the catalytic behavior of the lanthanide oxides is closely related to the properties of Ln^{3+} ions [1, 2]. In particular, for alcohol decomposition reactions, a regular variation of activity from La_2O_3 to Lu_2O_3, parallel to the ionic radius of Ln^{3+} is proposed 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.