Journal of Molecular Catalysis A: Chemical 418–419 (2016) 154–157

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

One pot synthesis of linear 1-alkylbenzenes from styrene, ethylene and hydrogen

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ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form 21 March 2016
Accepted 26 March 2016
Available online 28 March 2016

Keywords:
Polyinsertion catalysis
Ansa-metallocene
LAB
Styrene regiochemistry

ABSTRACT

Highly linear 1-alkylbenzenes can be obtained in mild conditions and with good selectivity, through the homogeneous catalysis of olefin polyinsertion from cheap and largely available reagents. The comparison among some ansa metallocenes shows that the coordinative framework of the catalytic metal, by regulating the regiochemistry of the styrene insertion, determines upon the selectivity of the reaction.

1. Introduction

The alkylbenzenes are widely used as intermediates for the production of detergents, their sulfonation giving rise to anionic surfactants of relevant commercial interest with a worldwide production of some millions of tonnes. Among the alkylbenzene sulfonates particular attention is paid to the linear ones due to the faster and more complete biodegradation that makes them preferable as eco-friendly products with respect to the branched ones. The synthesis of the alkylbenzenes is generally accomplished through benzene alkylation in a Friedel-Craft reaction by employing as reactants chloroalkanes or 1-alkenes, which in turn mostly are the products of the ethylene oligomerization. The overall process is complex involving different steps with intermediates fractionation and by-products removing [1,2].

While the Ziegler-Natta homogeneous catalysis has gained momentum as a powerful tool for the synthesis of a great number of different polymer and copolymer structures thanks to the widely tunable framework of the metallic complex, less investigated was the prospect of the formation of well-defined C—C bonds for the synthesis of smaller molecules of practical interest [3,4]. In this paper we report the investigation on the possible one-pot synthesis of LAB's starting from largely available commodities such as ethylene, styrene and hydrogen, in mild experimental conditions. The tool adopted to attain this goal is indeed the polyinsertion catalysis of the olefins, which, in its homogeneous variation, takes advantage of the large armoury of catalysts having different behaviours towards the title reagents both with respect to the relative reactivity of styrene, ethylene and hydrogen and with regard to the regiochemistry of the styrene insertion [5–7]. The latter aspect is crucial in order to avoid the formation of short branches that are detrimental for the biodegradability of the detergents.

2. Results and discussion

Keeping in the mind the idea of evaluating the feasibility of the title synthesis we have explored the behaviour of several group 4 metal complexes activated by methylalumoxane. At least in principle the target-molecules could be produced through two different catalytic pathways, as depicted in the Scheme 1.

Both routes should be taken into account because, as a general rule, the styrene insertion into the Zr-H bond is primary whereas the insertion into the Zr-C bond is secondary, in the absence of steric constraint [3].

The ability of a series of catalysts to produce linear alkylbenzenes was compared in the same experimental conditions. As a general procedure a stainless steel reactor with inside a sealed vial containing about 5 mg of the zirconocene complex was charged under nitrogen atmosphere with a solution of the co-catalyst (methylalumoxane, around 300 mg) dissolved in a mixture 7/13 v/v of styrene and toluene. The nitrogen atmosphere was removed and substituted with 1 MPa of hydrogen and with ethylene up to 2 Mpa. Then breaking the sealed vial started the reaction. In order to maintain a nearly constant composition of the reactants we stopped

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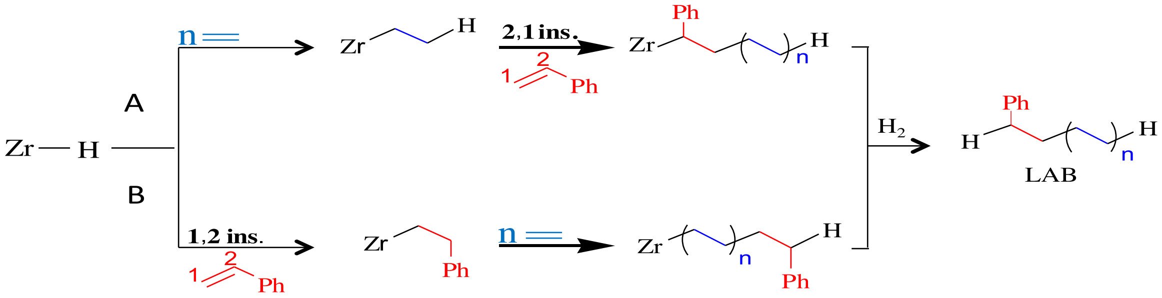
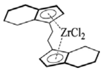
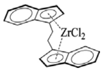
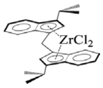
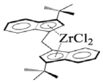
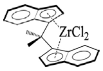
http://dx.doi.org/10.1016/j.molcata.2016.03.040
1381-1169/



Scheme 1. Alternative pathways for the synthesis of LAB.

Table 1
Comparison of the activities of different ansa-metallocenes.

Run[a]	Catalytic complex	Turnover[b] g/mmol	% LAB[c]	% α,ω diphenyl alkanes[c]
1		51	67	16
2		53	25	60
3		41	61	1
4		10	82	0
5		32	18	76
6		3	57	0

[a] The reaction parameters are described in the experimental section.
[b] The turnover is reported as grams of raw oil per mmol of the ansa-metallocene complex.
[c] The complement to 100 is due mainly to ethylene oligomers.

the reaction after one hour at low styrene, ethylene and hydrogen conversion.

The Table 1 shows the results of these experiments. In particular it is evidenced the composition of the products mixture, two main classes of compounds having different relevance: the linear alkylbenzenes and the $\alpha-\omega$ diphenyl alkanes; in addition a variable amount of paraffin arising from ethylene oligomerization.

On the basis of the previous studies on the regiochemistry of styrene insertion one could argue that the LAB's of run 3 and 4 are formed through the primary styrene insertion into the Zr-H bond followed by some ethylene insertion until the cutting of the metal-carbon bond by the molecular hydrogen (pathway B of scheme). This hypothesis is based on the unlikely secondary styrene insertion into the metal-carbon bond (pathway A) when the ansa zirconocene bears a bulky group linked to the carbon 3 of the coordinative framework. On the contrary when the secondary styrene insertion is not forbidden, as for the catalysts of run 1, 2, 5 and 6 the route A cannot be ruled out, at least in principle.

It's worth noting, on the other hand, that the $\alpha-\omega$ diphenyl alkanes, generally present as by-products, are by far the main components of the oil obtained in run 5. These structures arise, without ambiguity, from primary styrene insertion into the Zr-H bond followed by some ethylene insertions (or even none, in the case of the 1,4-diphenylbutane) and finally by secondary styrene insertion with cutting by hydrogen, when the catalytic site is presumably in a "dormant state".

The different distribution of the products above discussed is well represented by the two GC traces reported as exemplary in Fig. 1.

In particular one can observe that among the LAB's of run 1 (Fig. 1a) are prevalent those with aliphatic chain of ten or twelve carbon atoms, i.e. the more interesting for their use as surfactants, after sulfonation. In the other hand Fig. 1b displays the $\alpha-\omega$ diphenyl alkanes of run 5 as almost the only products with a decreasing trend starting from 1,4-diphenylbutane, i.e. the styrene hydrodimer.

When in the ansa-zirconocene complexes the two halves of the ligand are held together by one carbon atom, the steric encumbrance in carbon 3 of the coordinative frame seems mandatory in order to have a mixture of LAB's virtually free from $\alpha-\omega$ diphenyl alkanes (runs 3 and 4). This observation suggests that, at least for these kind of ansa-zirconocenes, the formation of LAB's proceeds through primary styrene insertion into the Zr-H bond followed by multiple ethylene insertions and finally hydrogen cutting. Such regiochemical considerations arise from what observed in styrene dimerization in presence of hydrogen where 1,3-diphenylbutane is practically the only product [5].

The raw oil obtained in run 1 has been analysed through ^{13}C NMR and the spectrum is reported in Fig. 2. One can observe that the only relevant signals are those assigned to the linear alkylbenzene structure and from the integration can be argued a main length of 14 carbon atoms in the aliphatic chain, in accordance with the GC evidences.