Alkanes

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Homologation of Propane Catalyzed by Oxide-Supported Zirconium Dihydride and Dialkyl Complexes**

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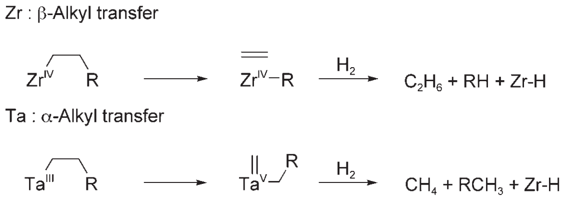
Zirconium hydrides supported on oxide materials catalyze several classical reactions, such as hydrogenation, reductive cyclization, cyclotrimerization, and olefin polymerization.[1–5] Notably, they also catalyze the hydrogenolysis of polyolefins and alkanes, *except ethane*, and this reaction corresponds to the reverse of the polymerization of olefins.[6–9] Under similar conditions, alkanes, *including ethane*, are transformed into their lower homologues in the presence of a catalytic amount of silica-supported tantalum hydride.[10] Cleavage of the carbon–carbon bond is different for both catalysts (Group 4 vs. Group 5): β-alkyl transfer for d^0 zirconium catalysts versus α-alkyl transfer for d^2 tantalum catalysts so that hydrogenolysis of a C–C bond in the skeleton of an alkane occurs by removal of one carbon atom at a time for tantalum catalysts and of at least two carbon atoms for zirconium catalysts, hence the difference in the selectivity of the final product (Scheme 1).[9,11,12]

Silica-supported tantalum hydrides also catalyze the conversion of alkanes into their direct lower and higher homologues. This reaction, named alkane metathesis,[13] involves carbene and metallacyclobutane intermediates,[14,15] and it explains the selective formation of the directly lower and higher linear homologues of the starting alkane through the transfer of one carbon atom at a time, thereby preventing the formation of long-chain alkanes. We have exploited the specific properties of Zr, which is able to 1) activate C–H bonds of alkanes through σ-bond metathesis, 2) carry out hydrogenolysis (the transfer of at least two carbon atoms through β-alkyl transfer), and 3) polymerize olefins by insertion.[16,17] Herein, we report on the transformation of propane into longer-chain higher homologues (up to C_{10}) at moderate temperatures.



Scheme 1. Mechanisms for β-alkyl (Zr^{IV} complexes) and α-alkyl (Ta^{III} complexes) transfer.

In an autoclave, zirconium hydride supported on silica–alumina was brought into contact with 500 equivalents of propane under supercritical conditions (43 bar, $d = 510\ \mathrm{Kg\,m^{-3}}$). After 48 h at 200 °C, 12.6 % of the propane was converted into lower (39.1 %) and higher homologues (60.9 %). Notably, the major product was 2-methylpropane (20.7 %), and overall branched higher homologues up to C_{10} are favored, and particularly the iso homologues, except for pentanes (see the Supporting Information, Table S1 for detailed selectivities). This selectivity is in contrast with that reported with tantalum hydride or tungsten hydride supported on oxide supports:[13,18] 1) linear higher homologues are the major products; 2) higher homologues are mainly butanes and pentanes along with trace amounts of hexanes.

The reaction was studied in a flow reactor to identify primary products by investigating the effect of inverse space velocity (contact time) on product selectivity.

First, using a constant flow of propane (600 kPa, 3 N mL) at 216 °C, we observed the formation of H_2, methane, and ethane, which resulted from the C–H bond activation of propane, and its subsequent hydrogenolysis (Supporting Information, Figure S1).[6] After 500 min, constant selectivities were obtained, and they are as follows (see Supporting Information, Figure S1): 22 % (methane); 40 % (ethane); 22 % (isobutane); 6.9 % (butane); 2.5 % (isopentane); 2.5 % (pentane); 2.0 % (homologues with at least six carbon atoms). The branched-to-linear ratio of higher homologues is similar to that observed in batch reactors (mainly branched alkanes). Additionally, when zirconium hydride supported on silica is used, similar selectivities are obtained: 23 % (methane); 39 % (ethane); 17 % (isobutane); 6.9 % (butane); 2.2 % (isopentane); 2.4 % (pentane); 3.6 % (homologues with at least six carbon atoms). The similarity of the values demonstrates that the support does not participate in the reaction.

Second, when the flow rate is changed over a wide range (0–8 $\mathrm{mL\,min^{-1}}$), conversion varies linearly with contact time (see Supporting Information, Figure S2), which indicates that chemical rates are being measured and that the extrapolated

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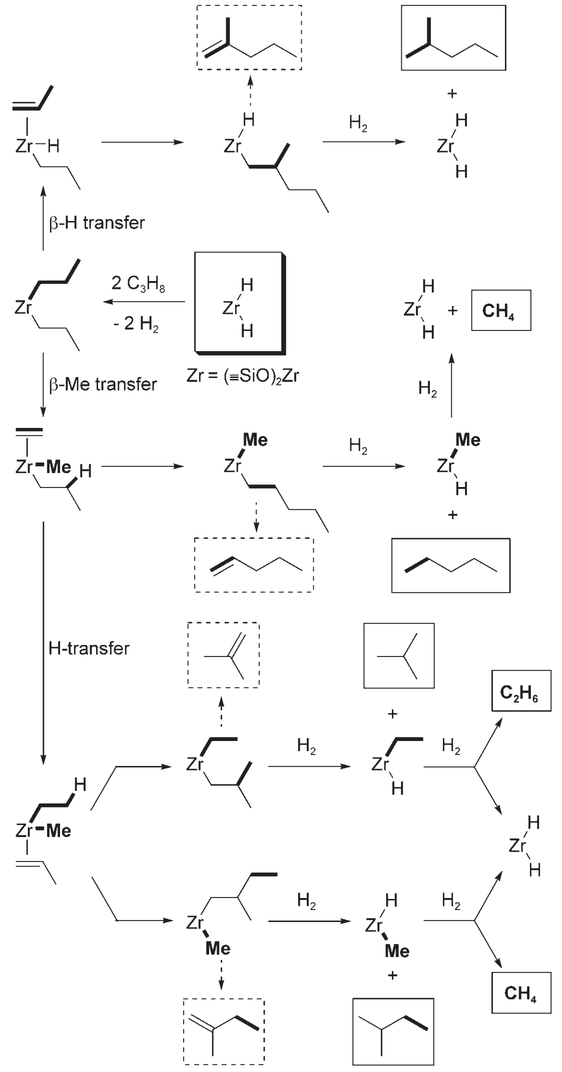
selectivities at zero contact time provide information about the reaction mechanism. The primary products are H_2 and olefins (C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, and C_6H_{12}), while alkanes are only secondary products (Supporting Information, Figures S3 and S4). Notably, the olefins are mainly branched, which is again in contrast with that observed in alkane metathesis with tantalum-based catalysts, for which the product distribution is characterized by the presence of mainly linear olefins.[13–15,19] The product selectivities in alkane metathesis are associated with the formation of the products by the carbene–olefin mechanism of Chauvin and Hérisson,[20] which explains the high selectivity for C_{n+1} homologues (1,3-disubstituted metallacyclobutanes are formed more readily than 1,2-disubstituted ones) and the low selectivity towards branched alkanes (highly disfavored formation of gem-disubstituted metallacyclobutanes).

In the case of the zirconium catalysts, this mechanism cannot explain the product distribution obtained. We therefore propose that the active species is a zirconium dihydride complex and that the mechanism of formation of the products involves the following elementary steps (Scheme 2): σ-bond metathesis (C−H activation and hydrogenolysis);[11,21,22] β-H and β-alkyl transfer[11,21] associated with intramolecular hydride transfer;[23] olefin insertion in the remaining alkyl chain leading to higher olefins (through β-H transfer) and alkanes (hydrogenolysis).[11,21,22]

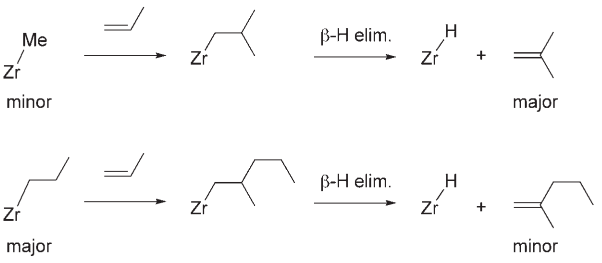
First, zirconium hydrides supported on silica and silica–alumina, respectively, are two different surface species, $[(\equiv SiO)_3ZrH]$ and $[(\equiv SiO)_2ZrH_2]$ (Supporting Information, Figure S5),[24] and C−H activation is faster on the more electrophilic dihydride species.[17] Second, the higher selectivity of isobutene compared to that of methyl-branched pentenes is not consistent with a simple insertion of adsorbed propene on Zr–alkyl species because the concentration of Zr–propyl has to be greater than that of Zr–Me species (Scheme 3). Therefore, the best way to explain the observed selectivities and primary products is that a dialkyl species is the propagating species (Scheme 2).

According to the mechanism depicted in Scheme 2, ethene and propene can be readily formed through primary processes, β-H and β-Me transfer, respectively, on the Zr–propyl propagating species. Pentenes and methylpentenes are obtained by the insertion of ethene or propene into adjacent Zr–propyl species and subsequent β-H elimination. However, the major process (formation of isobutene) requires a hydride transfer between the coordinated ethene and the Zr–propyl species, which leads to a surface complex of $[Zr(Me)(Et)(C_3H_6)]$. At this stage, propene can insert either into the methyl or into the ethyl branch to give, after β-H elimination, isobutene (the major product)[25] or isopentenes. Under catalytic conditions, H_2 (a primary product) is used to cleave the Zr–alkyl bond to generate alkanes (secondary products).

On starting with a well-defined supported Zr dineopentyl species,[26] the homologation of propane at 216 °C gives the same reaction products with slightly different selectivities: methane (30.5 %); ethane (42.3 %); isobutane (12.7 %); butane (5.7 %), which confirms the proposed dialkyl/hydride active sites.[27]



Scheme 2. Elementary steps in the formation of alkanes when $\{ZrH_2\}$ is the propagating species, Zr indicates $(\equiv SiO)_2Zr$. Primary products are highlighted in dashed boxes, reaction products in solid-line boxes. Bold bonds indicate the path of one C_3H_8 unit through the scheme.



Scheme 3. Formation of products from {ZrMe} and {ZrPr} species.

In conclusion, propane can be transformed at moderate temperatures (216 °C) into mainly higher-branched homologues when heated under supercritical conditions in the presence of a zirconium complex supported on oxide materials (silica and silica–alumina). Product selectivity and studies on inverse space velocity clearly show that the products are formed on dialkyl zirconium active sites by a reaction similar to the Ziegler–Natta olefin polymerization. The olefins are generated in situ on one of the alkyl branches (β-H or β-alkyl transfer) and inserted into the other, thus making a longer alkyl chain. This finding also explains the absence of olefin intermediates in the hydrogenolysis of alkanes catalyzed by silica-supported zirconium hydride and shows that the dihydride is the active site.

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[27] The starting MCM-41-supported alkyl zirconium species contains $>90\%$ $[(\equiv SiO)_2Zr(CH_2R)_2]$ ($R = t$Bu), while the silica–alumina- or silica-supported zirconium hydride contains only 30% of dihydride species, hence the difference in intrinsic inverse space velocity (number of active sites/flow rate), and thereby final product selectivities.