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Heterogeneous Dehydrogenation

Catalytic Dehydrogenation of Isopentane with Iridium Catalysts**

Helmut G. Alt and Ingrid K. Böhmer*

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

The catalytic activation of alkanes under mild conditions to give the corresponding alkenes and hydrogen[1] has tremendous industrial implications because olefins are the most important starting materials for large-scale industrial processes such as olefin polymerization, dimerization, oligomerization, hydroformylation, and metathesis. In the search for a process by which olefins can be produced from alkanes without a steam cracker, iridium complexes have proved to be the best catalysts so far.[2–5] An iridium catalyst with a pincer ligand was reported to give the best performance,[6] but it had the big disadvantage that an added external olefin was required to eliminate the formed hydrogen from the equilibrium. The addition of such "sacrificial olefins" is not economic and limits the commercial value of the process. Catalysts that do not need a "sacrificial olefin" are rare,[7,8] and typically they perform poorly in homogeneous solution.

We found that a series of iridium complexes, in combination with phosphorus-containing compounds on silica gel as the support material, are able to activate alkanes in a fixed-bed reactor to give the corresponding alkenes and hydrogen with high selectivity and high activity. As a model compound we chose isopentane, a refinery product with a high octane number of 92, which cannot be added to gasoline because of its low boiling point of 28 °C.

We tested four different iridium complexes and found a drastic dependence of the activity on the number of phosphine ligands (Figure 1). The activity of H_2IrCl_6 for isopentane activation could be increased significantly when external PPh_3 was added to the reaction mixture. In addition, the activity increased overproportionally at temperatures higher than 350 °C (see Figure 2). This behavior indicates the formation of a new catalytic species at 350 °C that is more active than the original one.

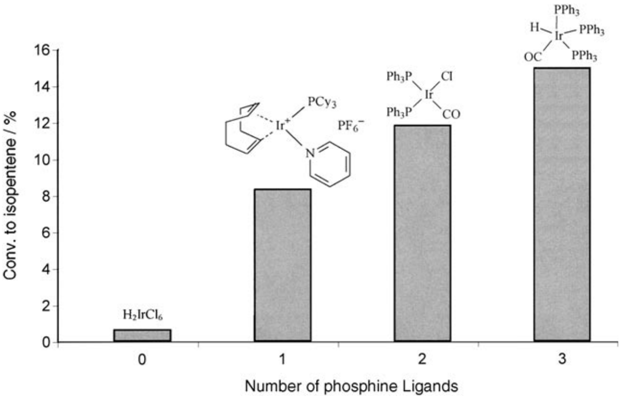


Figure 1. Correlation between the number of phosphine ligands and the activity of the catalyst for the dehydrogenation of isopentane at 400 °C.

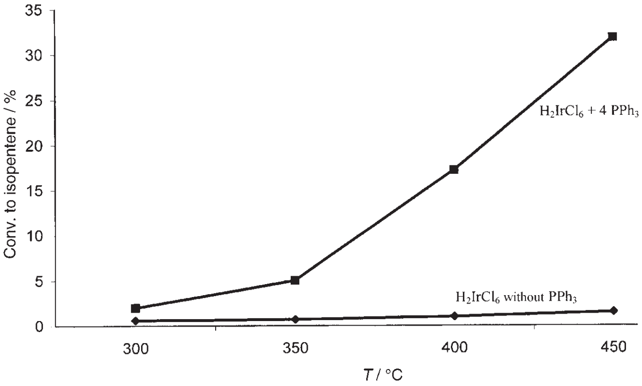
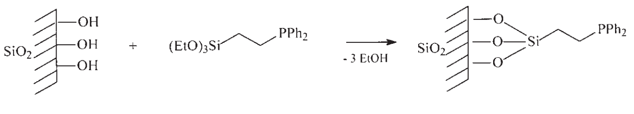


Figure 2. Comparison of the activity of H_2IrCl_6 on silica gel without PPh_3 and with 4 equiv PPh_3 depending on the reaction temperature.



Scheme 1. Functionalization of the silica gel surface (also see the Experimental Section).

In another experiment we used the phosphine-free catalyst bis(1,5-cyclooctadiene)iridium(I) tetrafluoroborate on silica gel. In addition, catalysts with Ir/P ratios of 1:4 and 1:8 ratio were synthesized. Instead of an externally added triphenylphosphine, the phosphine could also be integrated into the catalyst through functionalized silica gel (see Scheme 1). All of these catalysts were tested and compared in C–H activation experiments (Figure 3). The conversion at 450 °C increased from 2.3 % to 21.9 % when a fourfold excess of triphenylphosphine was added. The higher Ir/P ratio of 1:8 improved the conversion to 26.1 %. A catalyst with phosphine-functionalized silica gel (Ir/P 1:4) also improved the conversion of isopentane by threefold to 9.8 % at 450 °C.

The GC detection of reaction products containing phenyl groups led to the assumption that the organometallic

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[*] Prof. Dr. H. G. Alt, I. K. Böhmer
Laboratorium für Anorganische Chemie
Universität Bayreuth
Universitätsstrasse 30, 95440 Bayreuth (Germany)
Fax: (+49) 921-55-2044
E-mail: helmut.alt@uni-bayreuth.de

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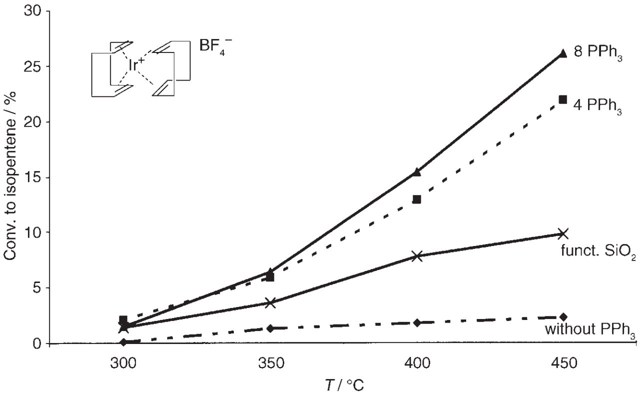

Figure 3. Comparison of conversion rates of catalysts with and without triphenylphosphine.

complexes decompose partly at elevated temperatures by losing the phenyl groups of triphenylphosphine; similar results were found previously for other iridium catalysts.[7] To test this for the systems with externally added phosphines, the carbon and phosphorus contents of three catalysts before and after the reactions were analyzed (see Figure 4).

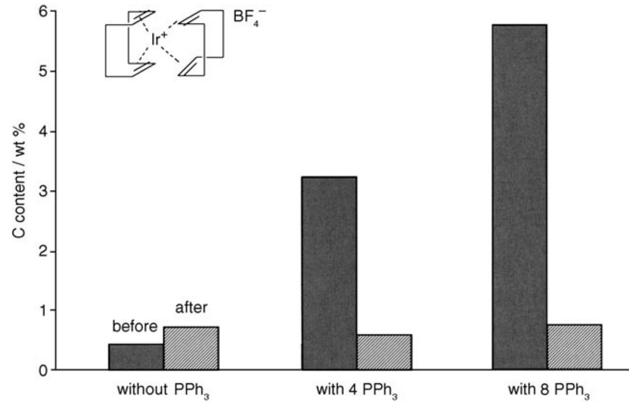

Figure 4. Carbon content of dehydrogenation catalysts before (black) and after the reaction (shaded).

The data are interesting in a number of aspects. First of all, they show that the main carbon content, presumably due to triphenylphosphine, disappears during the reaction. This confirms the assumption of the loss of phenyl groups. Apparently this loss does not affect the activity in a negative way: it was detected by thermogravimetric analysis (TGA) at temperatures below 400 °C, whereas the maximum conversion occurs at higher temperatures. This could mean that the loss of the phenyl groups is required for the formation of a more active species. Completely phosphine-free catalyst systems had lower conversion rates. All investigated catalysts maintained their high activities over days, indicating that the eliminated phenyl groups from the triphenylphosphine ligands or additives cannot play the role of hydrogen-consuming ("sacrificial") components. We also found that the amount of coking on the active catalysts is negligibly low. Therefore this should not be the reason for deactivation.

If one compares the phosphorus content of the catalyst systems before and after the reactions, a strong dependence between iridium and phosphorus is apparent. This indicates that the phenyl groups are lost but the phosphorus content before and after the run is about the same. After the reaction with an Ir/P ratio of 1:8, a slight loss of phosphorus is apparent, but this can be expected owing to an insufficient interaction of phosphorus with the metal.

To gain further insight, we conducted the dehydrogenation of isopentane for 5 h in a fixed-bed reactor at 150, 250, 350, 450, and 550 °C. After the runs, the carbon and phosphorus contents of the samples were analyzed. A small amount of PPh_3 was lost at room temperature. It is remarkable that the P/Ir ratio drops to a value of 3:1, which remains constant above 250 °C. At this temperature a drastic loss of the phenyl groups takes place, which is evident from the decreasing C/P ratio. This value drops below 18, which would be expected for intact PPh_3 groups. It is not possible to use the carbon contents as absolute values owing to the amount of cyclooctadiene in the catalyst, leads to a value higher than 18 in the first samples. Above temperatures of 500 °C coking becomes evident. The thermodynamic equilibrium of the dehydrogenation of isopentane can be calculated with computer software (Aspen or HSC). Figure 5 shows two curves that are not identical. However, the experimental results (29.9 % yield at 450 °C) fit the predictions very well.

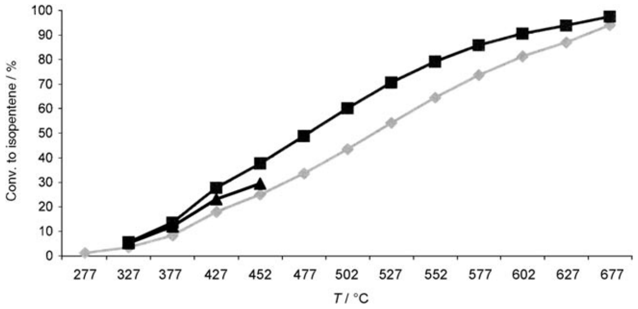

Figure 5. Calculation of the thermodynamic equilibrium of the dehydrogenation reaction of isopentane at different temperatures (light gray: Aspen, dark gray: HSC Chemistry, black: experimental results).

The actual catalyst is probably an iridium phosphide or an iridium–phosphorus cage or nanocluster. These conclusions are based on comparative measurements between active and less active catalysts before and after the dehydrogenation reaction. Less active catalysts showed bigger conglomerates of iridium metal that formed during the reaction and are apparently not able to activate CH bonds. Since the dehydrogenation reaction is an endothermic equilibrium reaction, it is advantageous to perform this as a continuous reaction in a fixed-bed reactor at high temperatures and to separate the products. The same reactions in a batch reactor (closed system) gave much lower yields.

Experimental Section

The catalysts were synthesized by supporting different metal complexes on silica gel by the method of “incipient wetness”. This impregnation method maximizes the dispersion on the surface. First, the amount of liquid absorbable by the support was determined. For example, toluene was added dropwise to one gram of silica (Davicat SI 1102) until the liquid was visible around the particles. The required amount of solvent could be calculated by the weight difference. A metal complex (H_2IrCl_6, $[(cod)_2Ir]^+BF_4^-$, $[(cod)(PCy_3)Ir(py)]^+PF_6^-$, $[(PPh_3)_2Ir(Cl)(CO)]$, or $[(PPh_3)_3Ir(H)(CO)]$) was dissolved in exactly the amount of a suitable solvent (THF, toluene, CH_2Cl_2, water) that was required to fill all pores of the support. The solution was added dropwise to the support material and the supported catalyst was dried under a nitrogen stream, by heating, and/or under high vacuum.

The metal content on the support was in a range of 0.3–1.0 wt %. To examine the influence of triphenylphosphine on the activity of the metal complexes, 4 or 8 equiv of triphenylphosphine was dissolved in *n*-pentane and added to the supported catalyst by the technique of “incipient wetness”. In experiments with $[(cod)_2Ir]^+BF_4^-$ the silica gel support was functionalized with phosphine groups before use. The silica gel surface can be modified by the reaction of its surface hydroxy groups with bifunctional linker agents[9–12] (see Scheme 1). For this reaction, a solution of 2-(diphenylphosphanyl)ethyltriethoxysilane (188 mg) in pentane (7.2 g) was added dropwise to silica gel (6.0 g). The impregnated silica gel was heated to 120 °C for 3 h under nitrogen. After the support had cooled to room temperature, a solution of $[(cod)_2Ir]^+BF_4^-$ was added by the technique of “incipient wetness”.

All synthesized catalysts were tested in a fixed-bed reactor for the dehydrogenation of isopentane without additional activation steps and without a “sacrificial olefin”. The catalysts were analyzed before and after the C–H activation experiments by combustion analysis (ConocoPhillips Inc., Bartlesville, USA) for the content of carbon, hydrogen, and phosphorus.

For C–H activation experiments, a sample of the catalyst (5 g) was placed in a stainless-steel reactor tube and held in place by layers of glass wool and glass beads. The packed reactor was plumbed into a pipe system inside of a heating unit. After the system had been purged with nitrogen and heated to 300 °C, the feed isopentane was pumped up-flow by a syringe pump with a weight hourly space velocity (WHSV) of 1.9 through the catalyst bed. The pressure was about 0.1 bar. The reaction temperature range was from 300 to 450 °C, measured by a thermocouple positioned in the catalyst bed. The products were collected in a sample collector cooled with ice. Samples were removed hourly and the products identified by GC. Depending on the temperature, an isomeric mixture of 2-methyl-2-butene, 2-methyl-1-butene, and 3-methyl-1-butene was generated. To calculate the activity, the sum of the three isomers was used. The activity for the dehydrogenation reaction is denoted as conversion of isopentane to isopentene in percent.

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