Influence of triphenylphosphine on the activity of heterogeneous iridium, rhodium and platinum containing catalysts for the dehydrogenation of saturated hydrocarbons

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ABSTRACT

A series of heterogeneous iridium containing catalysts was synthesized by the incipient wetness method. The support material was silica gel. The heterogeneous catalysts were able to dehydrogenate isopentane to isopentene with very high activities and selectivities. The use of external additives (e.g. PPh_3) in case of the heterogenized iridium complex $IrH(CO)(PPh_3)_3$ increased the conversion of isopentane up to 30%. Such a conversion rate has been predicted by model calculations of the thermodynamic equilibrium of the dehydrogenation reaction of isopentane.

1. Introduction

One of the most attractive goals in modern chemical research is to find catalysts that are able to activate saturated hydrocarbons. The ubiquitous nature of saturated CH bonds implies that the ability to convert aliphatic CH bonds into other functional groups would significantly multiply the potential applications of hydrocarbon feedstocks and their commercial values.

The key step of CH activation reactions is the formation of an electronically and coordinatively unsaturated species to enable the oxidative addition of an alkane to the metal center. In a second step, β-hydrogen elimination can be induced either thermally or photochemically to produce the olefin and hydrogen in the catalytic cycle. The use of organometallic compounds offers the possibility to influence the properties of the metal center by various ligands. These ligands influence the metal center in a way that β-hydrogen elimination and simultaneous formation of the alkene ligand are facilitated.

Several research groups work in this challenging field of CH activation chemistry with organometallic catalysts [1–17]. The number of catalytic cycles that could be obtained with these systems is still very limited and another big disadvantage in most cases [18,19] is the necessary application of a "sacrificing olefin" like *tert*-butylethylene in order to shift the equilibrium of the reaction to the right side.

In refineries, the conversion of pentane or isopentane to the corresponding olefins and hydrogen is an attractive goal because these C_5-alkanes cannot be added to gasoline due to their low boiling points (36 and 28 °C). The corresponding alkenes, however, can be dimerized or trimerized catalytically and then be applied as gasoline or diesel components. Platinum or iridium metal impregnated supports are used for such commercial dehydrogenation processes. At temperatures of 610 °C a conversion of isopentane to isopentene up to 50% can be obtained, but the selectivity for this reaction is only 91% and the lifetime of the catalyst is less than five hours. High temperatures are required to enable endothermic CH activation reactions in sufficient yields but shorten the product selectivity and the lifetimes of the catalysts.

After previously published results [20–25] we report now the heterogenization of various complexes of iridium, rhodium and platinum leading to efficient dehydrogenation catalysts for isopentane and other hydrocarbons.

2. Experimental

The catalysts have been synthesized by supporting different metal complexes on silica by the method of incipient wetness. This

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impregnation method maximizes the dispersion on the surface of the support material.

First, the amount of liquid absorbable by the support had to be determined. For example, to one gram of silica, toluene was added dropwise until the liquid was visible around the particles. The required amount of solvent could be calculated by the weight difference.

The organometallic compound 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 dried with a nitrogen stream, heat and/or under high vacuum. The used silica was silica Davicat© SI 1102. As metal complexes the following compounds have been used: $H_2IrCl_6 \cdot nH_2O$ (**1**), $[(cod)_2Ir]^+BF_4^-$ (**2**), $[(cod)(P(C_6H_6)_3)Ir(Pyr)]^+PF_6^-$ (**3**), $[(PPh_3)_2Ir(Cl)(CO)]$ (**4**), $[(PPh_3)_3Ir(H)(CO)]$ (**5**), $H_2PtCl_6 \cdot nH_2O$ (**6**), $[(PPh_3)_2Rh(Cl)(CO)]$ (**7**), $[(PPh_3)_3Rh(H)(CO)]$ (**8**). (For an overview of all synthesized catalysts see Table 1.)

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, a four to eight molar ratio of triphenylphosphine dissolved in *n*-pentane was added by incipient wetness to catalysts no. **1**, **2** and **6** resulting in catalysts: $xH_2IrCl_6 \cdot nH_2O + 4 \times PPh_3$ (**9**), $[(cod)_2Ir]^+BF_4^- + 4 \times PPh_3$ (**10**), $[(cod)_2Ir]^+BF_4^- + 8 \times PPh_3$ (**11**), $xH_2PtCl_6 \cdot nH_2O + 4 \times PPh_3$ (**12**). Additionally, the silica was functionalized with phosphine groups before its use as support material for $[(cod)_2Ir]^+BF_4^-$. The silica surface can be modified by the reaction of its surface hydroxyl groups with bifunctional linker agents [26–35] (see Scheme 1).

For this reaction, a solution of 188 mg of 2-(diphenylphosphino)ethyltriethoxysilane in 7.2 g of pentane was added dropwise to 6.0 g of non-pretreated silica. The impregnated silica was heated to 120 °C for 3 h under nitrogen. After cooling to room temperature a solution of $[(cod)_2Ir]^+BF_4^-$ was added by incipient wetness (catalyst **13**, ratio Ir:P = 1:4).

All synthesized catalysts were tested for CH activation experiments in a fixed bed reactor for the dehydrogenation of isopentane without additional activation steps and without a "sacrificing olefin". The catalysts were analyzed before and after the CH activation experiments by combustion analysis for the content of carbon, hydrogen and phosphorus. The analyses were carried out at ConocoPhillips Inc., Bartlesville, USA.

For CH activation experiments, 5 g of the corresponding catalyst were placed in a stainless steel reactor tube, fixed by layers of glass wool and glass beads. The packed reactor was plumbed into a pipe system inside of a heating unit. After purging the system with nitrogen and heating to 300 °C, the feed isopentane was pumped up-flow via a syringe pump with a weight hourly space velocity (WHSV) of 1.9 through the catalyst bed. The pressure was about 1 psig. The reaction temperature range was from 300 to 450 °C, measured by a thermocouple positioned in the catalyst bed. The temperature was raised every 2 h in steps of 50 °C. The products were collected in a sample collector cooled with ice. Samples were taken hourly and the products identified with GC.

The activity for the dehydrogenation reaction is denoted in conversion of isopentane to isopentene in percent. Depending on the temperature, an isomeric mixture of 2-methyl-2-butene, 2-methyl-1-butene and 3-methyl-1-butene was generated. For the calculation of the activity, the sum of the three isomers was used. Additionally, the turn over frequency (TOF) is a useful indicator for the activity of a catalyst.
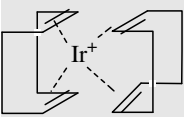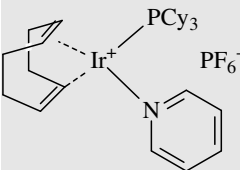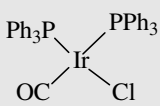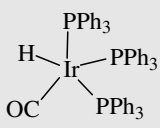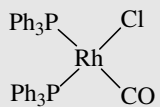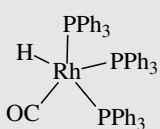
3. Results and discussion

3.1. Activity of different iridium complexes supported on silica

At elevated temperatures most organometallic complexes decompose to the metal and organic compounds. Catalytic activities at temperatures above 300 °C are mostly attributed to special properties of metals. When these assumptions are true, various iridium complexes, supported on silica, should show very similar activities. To examine this context, catalysts **1**, **3**, **4** and **5** were used for the dehydrogenation of isopentane in a fixed bed reactor at 400 °C. The obtained conversions to the alkene are shown in Fig. 1.

Depending on the organometallic compound used for the synthesis of the catalyst, the activities varied very much from 0.6% (**1**) to 15% (**5**) conversion of isopentane. It made no difference whether or not the structure of the organometallic species was neutral or ionic. Representatives of both types could effect low and high conversions, depending on the organic ligand system.

Iridic acid on silica (**1**) was almost inactive with a conversion of 0.6% isopentane to isopentene at 400 °C. The highest conversion and TOF was obtained with hydridocarbonyltris(triphenylphos-

Table 1
Synthesized catalysts

Metal complex	Catalyst no.	External phosphine	Molar ratio M:Ph
$H_2IrCl_6 \cdot nH_2O$	**1**		
	9	PPh₃	1:4
	2		
	10	PPh₃	1:4
	11	PPh₃	1:8
	13	funct. silica	1:4
	3		
	4		
	5		
$H_2PtCl_6 \cdot nH_2O$	**6**		
	12	PPh₃	1:4
	7		
	8		

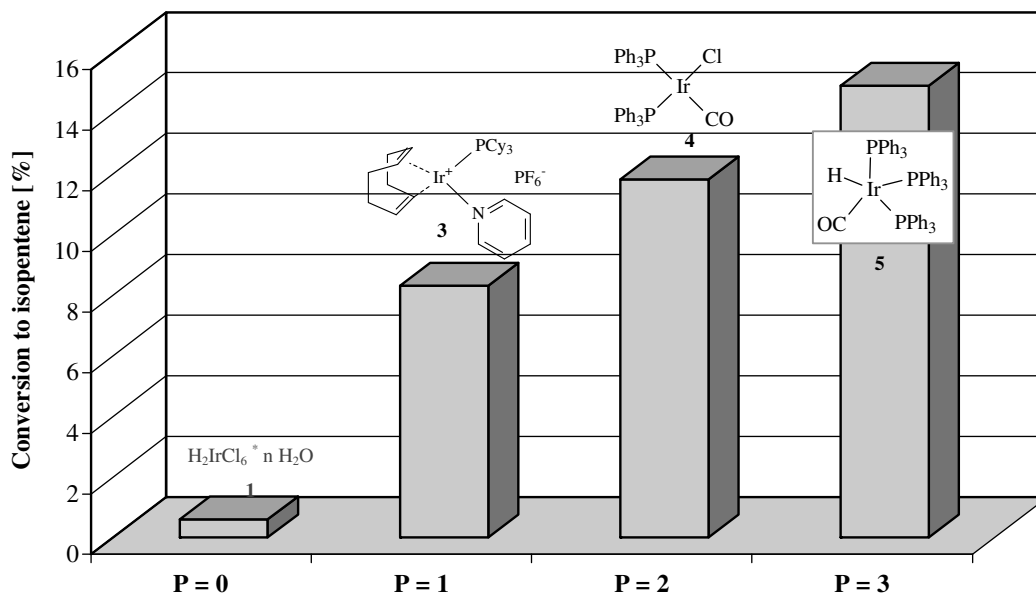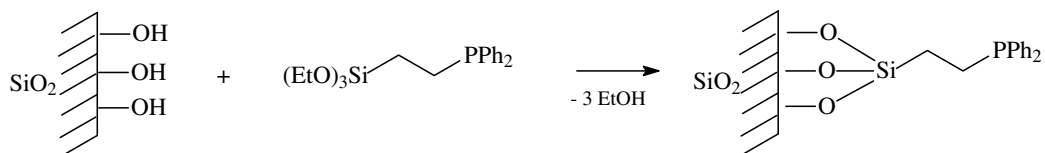**Scheme 1.** Functionalization of the silica surface.

Fig. 1. Correlation between the number of phosphine ligands and the activity of the corresponding catalyst at 400 °C (isopentane as feed).

phine)iridium(I) on silica (**5**). The TOF per hour was 290 and the conversion rate 15% with a selectivity of 98%.

It is noticeable that there is a direct correlation between the number of phosphine ligands in the complex and the activity. The biggest step is the introduction of one phosphorus containing component (catalyst **1**).

3.2. Influence of externally added triphenylphosphine on the activity

If the activity of dehydrogenation catalysts depends mainly on the presence of phosphines, the activity of less active catalysts should be increased by the addition of triarylphosphines to the catalysts. To examine this hypothesis, a 1:4-molar ratio of triphenylphosphine
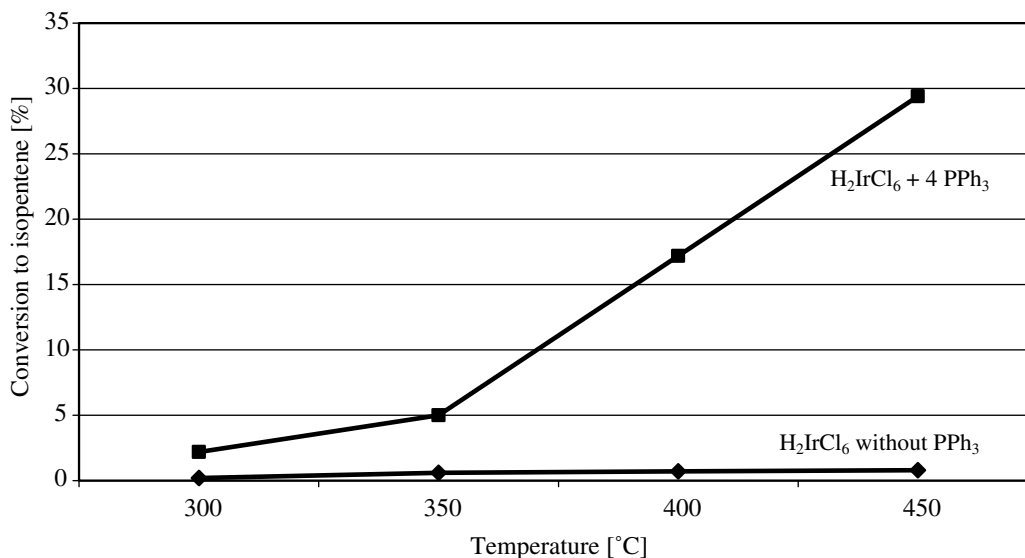

Fig. 2. Comparison of the activity of iridic acid on silica with and without various amounts of PPh_3.

was added to iridic acid on silica and the obtained catalyst was applied for CH activation reactions. The results are shown in Fig. 2.

The effect of the externally added phosphine on the CH activation behaviour is enormous. The conversion at 450 °C was only 0.8% with iridic acid as catalyst but 29.4% with triphenylphosphine as additive. This value is in the area of the thermodynamic equilibrium.

In addition, the life time of the catalyst was increased at higher temperatures.

To examine if this effect depends on a special type of organometallic compound, similar experiments were conducted with the cationic bis(1,5-cyclooctadiene)iridium(I)-tetrafluoroborate (see Section 3.3).

3.3. Comparison of the activities of catalysts 2, 10, 11 and 13

For comparisons, a phosphine free catalyst with bis(1,5-cyclo-octadiene)iridium(I)-tetrafluoro-borate on silica was used (2). Besides the 1:4 (Ir:P) ratio (10), a catalyst with a 1:8 ratio (11) was synthesized. Instead of an externally added triphenylphosphine, the phosphine was integrated into the catalyst via functionalized silica (13). All these catalysts were applied for CH activation experiments and compared with each other. The graphical comparison of the obtained data is shown in Fig. 3.

Compared with the experiments of iridic acid on silica, the influence of the externally added triphenylphosphine to the organometallic complex is high. The maximum conversion of 2.3% at 450 °C (catalyst 2) was increased to 21.9% by adding a four times excess of triphenylphosphine (10). A higher ratio of iridium to phosphorus of 1:8 brought another improvement of the conversion with additional 4.2% up to 26.1% (11).

Catalyst 13 with the phosphine-functionalized silica (ratio Ir:P = 1:4) increased the conversion of isopentane compared with catalyst 2 as well, but "only" to 9.8% at 450 °C. It is at least an enhancement of 300%. Triphenylphosphine on silica without a metal containing component did not show any catalytic activity.

3.4. Comparison of the activity of iridic acid and platinic acid

According to the literature, platinum can be stabilized by adding small amounts of other metals like iridium to the support [36–38]. In a series of experiments these two metals were com-bined in different ratios on silica Davicat® SI 1102 and the results were interpreted.

For the synthesis of the catalysts, iridic acid and platinic acid were used. A molar ratio of a four times excess of triphenylphosphine was added. The catalysts were used for CH activation reactions of isopentane.

At first, a comparison of the activities of separate catalysts with different metals was made (Fig. 4).

The iridium catalyst was more active in all temperature ranges. The content of iridium in this case was 0.53% on silica, the platinum content was 0.94% on silica. Therefore the difference in the TOFs was even higher.

The following Table 2 shows the data obtained with the experiments of the used mixtures of iridic and platinic acid on silica.

The data show that a combination of the two metals gave catalysts with higher activities than any of the metals alone. Iridium increased the activity of platinum in the same way as vice versa. The next figure elucidates this context with the conversion data at 400 °C (Fig. 5).

The diagram gives a clear picture of the enhancement of the activity combining iridium and platinum containing components on silica. The maximum conversion of 15.2% at 400 °C was obtained in the experiment with an Ir:Pt ratio of 4:1.

3.5. Investigation of the active species – analytical data

The experimental data proved the important influence of phosphine ligands on the activity of the dehydrogenation catalysts. The educts used for the preparation of the catalysts are known, but neither the state of the organometallic compounds on the support nor the catalytically active species. To optimize the developed system and to weed out existing problems, it is necessary to determine the responsible parameters.

Reaction products of phenyl groups in the GC spectra lead to the assumption that the organometallic complexes decompose partly at elevated temperatures by losing these aromatic groups of the triphenylphosphine. To examine this observation for the systems with externally added phosphines, the carbon and phosphorus contents of three catalysts (2, 10 and 11) before and after the experiments were analyzed (Fig. 6).

The data are interesting in different aspects. First of all they show that the main carbon contents, presumably coming from
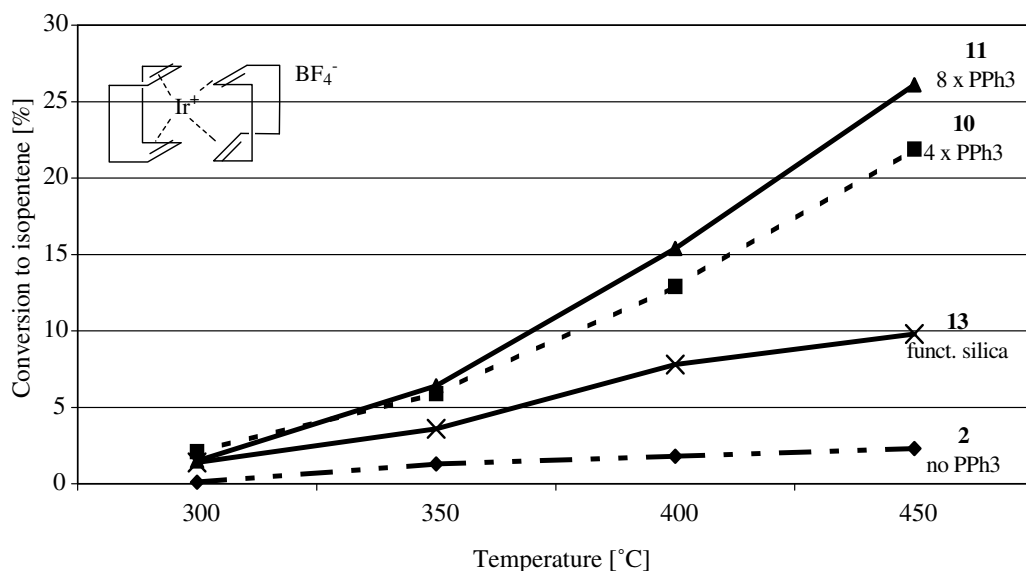

Fig. 3. Comparison of conversion rates of catalysts with and without various amounts of phosphines.
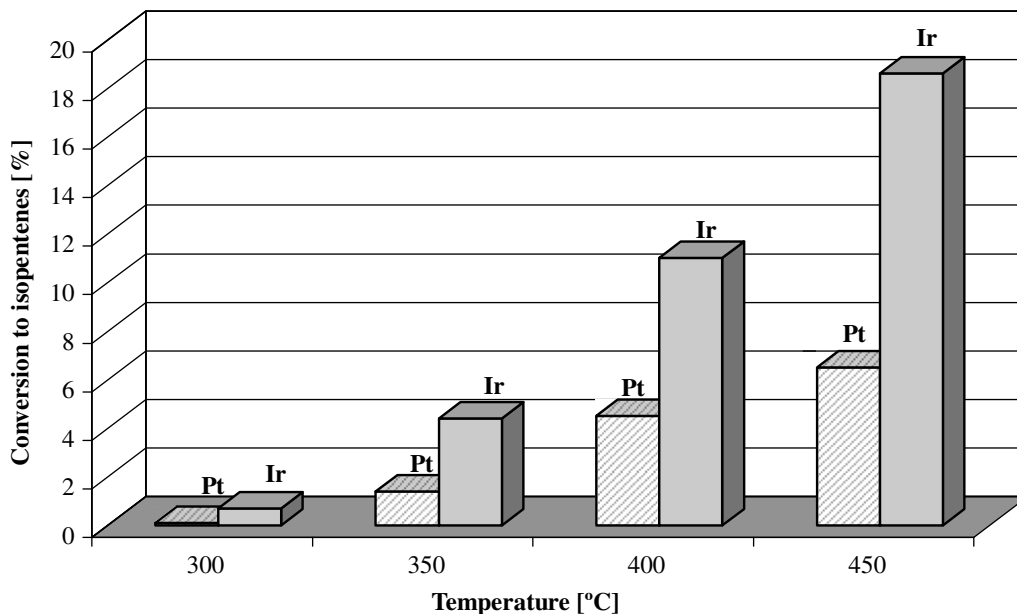
Fig. 4. Comparison of the activity of iridic acid/platinic acid with PPh₃ in the catalytic conversion of isopentane to isopentene.

Table 2
Experiments with different ratios of iridium and platinum on the same support

Exp. no.	Ir (% on silica)	Pt (% on silica)	$T = 300\ °C$		$T = 350\ °C$		$T = 400\ °C$		$T = 450\ °C$	
			Conv. (%)	TOF (h)	Conv. (%)	TOF (h)	Conv. (%)	TOF (h)	Conv. (%)	TOF (h)
68	0.53	0	0.7	7	4.4	46	11.0	103	18.6	167
74	0.4	0.1	1.2	16	7.5	81	15.2	174	23.7	255
75	0.25	0.25	0.8	12	5.9	88	12.6	172	18.4	253
76	0.1	0.4	0.3	3	2.8	30	7.4	78	9.9	86
72	0	0.94	0.1	0.3	0.2	1.0	4.5	27	6.5	36

the triphenylphosphine, disappears during the experiment. This confirms the assumption of the loss of phenyl groups. It probably does not affect the activity in a negative way because this loss was detected via TGA at temperatures below 400 °C. The maxi-

mum conversion occurs at higher temperatures. This could mean that the loss of the phenyl groups is required for the formation of the active species. Completely phosphine free catalyst systems had lower conversion rates.

Another information of this data is the fact that the amount of coking of active catalysts is negligibly low. Therefore this should not be the reason for deactivation.

Regarding the data of the phosphorus contents before and after the experiments (Fig. 7), it is obvious that there is a strong interaction between iridium and phosphorous in the corresponding catalyst systems. It proves the loss of the phenyl groups but not of the whole triphenylphosphine. The phosphorus content before and after the run is about the same. It is a little bit lower after the experiment with a ratio of Ir:P = 1:8 but this can be expected due to an insufficient interaction of phosphorus with the metal.
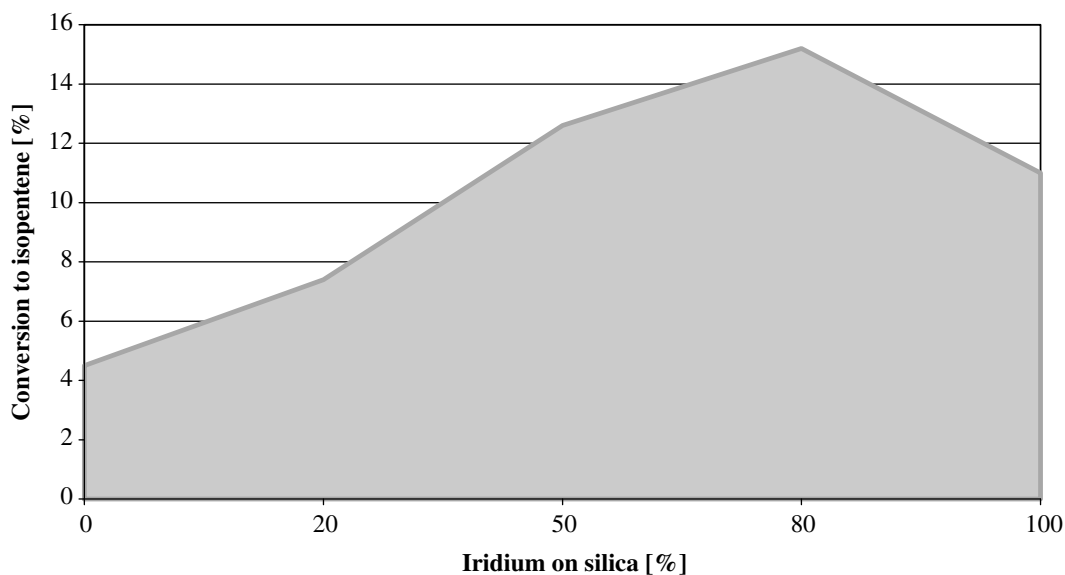

Fig. 5. Activity of mixed catalyst (Ir/Pt) systems for the dehydrogenation of isopentane at 400 °C.
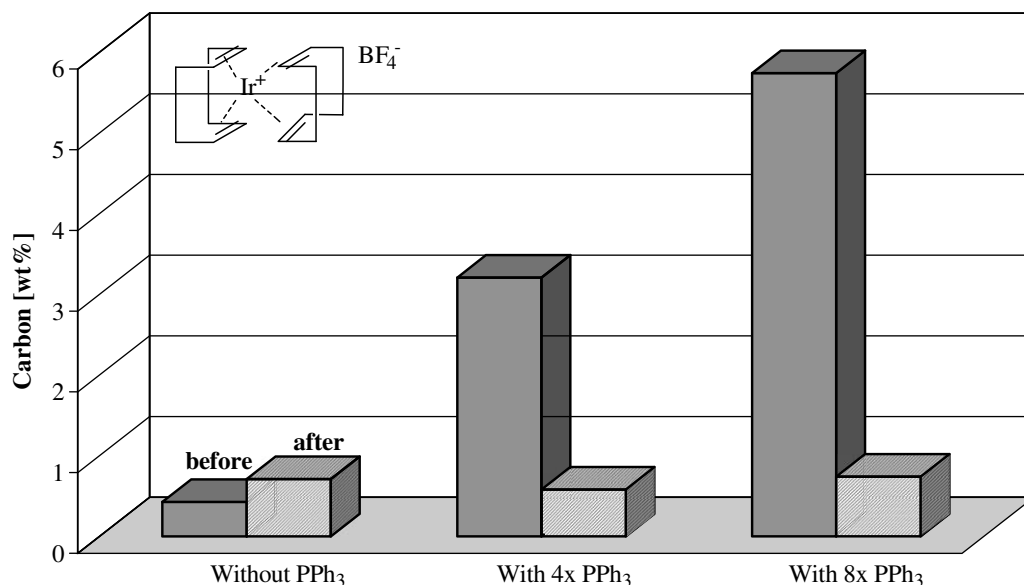
Fig. 6. Carbon contents of catalysts **2**, **10** and **11** before and after the run.
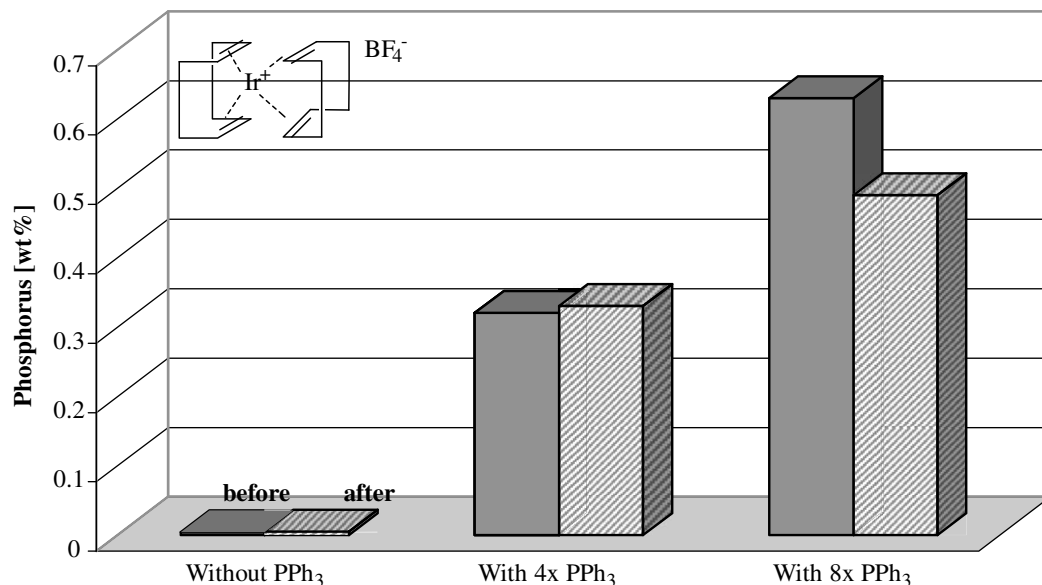

Fig. 7. Phosphorus contents of catalysts **2**, **10** and **11** before and after the runs.

To look into these important facts, another series of tests has been conducted with catalyst **11**: 5 g samples of **11** were applied for 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 (see Fig. 8).

A small amount of PPh₃ was lost at room temperature. It is remarkable that the P:Ir ratio drops to a value of 3:1 which is consistent above 250 °C. At this temperature a drastic loss of the phenyl groups takes place, visible at the decreasing ratio C/P. This value drops below 18 which would be expected for intact PPh₃ groups. It is not possible to use the carbon contents as absolute values due to the amount of COD in the catalyst which effects a higher value than 18 in the first samples. Above temperatures of 500 °C coking becomes visible.

Further attempts to find out more information about the changes of the catalyst systems before and after the reaction were made by photon energy measurements, absorption experiments with CO and XRD.

3.5.1. Photon energy measurement

Elements in different oxidation states absorb different photon energies. Therefore this method can be used to determine the oxidation states of elements.

The photon energy absorption of phosphorus compounds with phosphorus in the oxidation states 0, +1, +3 and +5 was measured to obtain the calibration line (Fig. 9). The fresh catalyst **10** (39329–33) and the used catalyst **10** after the experiment (39328–32) were measured, too. The results showed an oxidation state of +1.3 in the
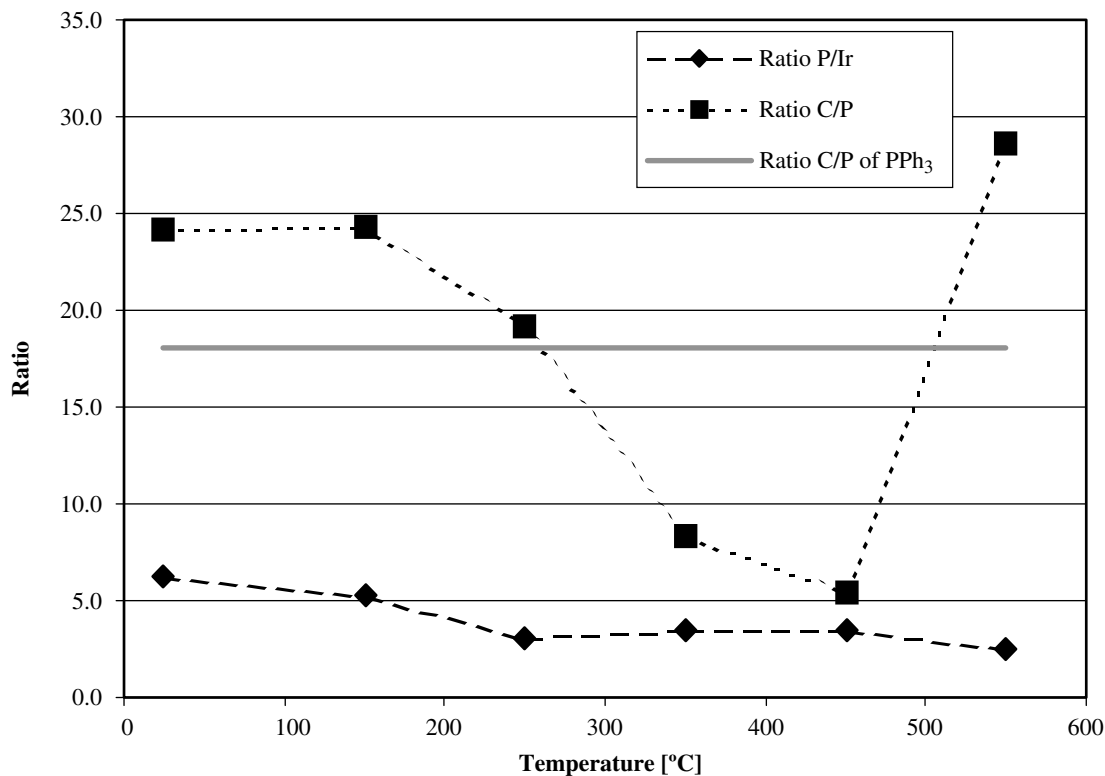
Fig. 8. Carbon and phosphorus contents of catalyst **11** at different temperatures.
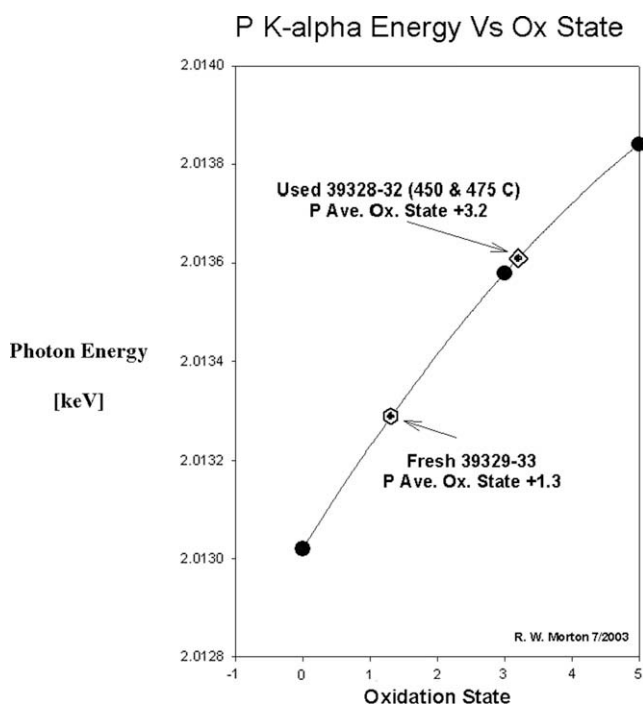

Fig. 9. Photon energy data of phosphorus in various oxidation states.

starting phase and +3.2 during the reaction indicating an oxidation process.

3.5.2. Adsorption experiments with CO

During the CH activation experiments, the operating catalyst system is not only exposed to the alkane but also to the alkene and the generated hydrogen forming a reducing atmosphere. Theoretically, it is very likely that iridium is reduced to iridium metal under these conditions, the present hydrogen and the high temperatures.

Iridium metal adsorbs CO if it is exposed to CO atmosphere. To examine whether the organometallic catalyst is reduced during the CH activation reaction or not, the following experiment was carried out: After simulation of the reaction conditions by heating up the catalyst to 450 °C under hydrogen atmosphere, the system was cooled to room temperature and exposed to carbon monoxide. The absorption of CO was then measured via IR spectroscopy. To see differences between catalysts with high and low activities, two systems were used for the experiment: the hydridocarbonyl-tris(triphenylphosphine)iridium(I) catalyst (high activity) and the chloro-1,5-cyclooctadiene iridium(I) dimer catalyst (low activity).

The spectra are shown in Fig. 10.

Both catalysts absorbed CO indicating that reduction to iridium(0) took place. But the energy of the CO bands is not identical. The one of the active catalyst is shifted to lower energy compared to the band of the catalyst with low activity. This is a hint of a different structure of the metal on the support. Two bands in common scale at the right side of the figure confirm this situation: The band of the low active catalyst is much smaller than the one of the active catalyst. Much less CO has been absorbed indicating that the metal is not distributed as well as the metal of the active catalyst. The excellent dispersion could be the reason for the high activity of the system.

3.5.3. X-ray diffraction results

Similar arguments could be obtained by looking at the XRD spectra. Two different catalysts, one with high and one with low activity, were measured before and after the experiment in the reactor to determine changes. The active catalyst was [Ir(COD)$_2$]-$^+$BF$_4^-$ with externally added PPh$_3$ (4× excess, cat. no. **10**). As low active species iridic acid on silica (cat. no. **1**) was used.

The spectra in the following figures show an overlap before (B) and after the run (A).
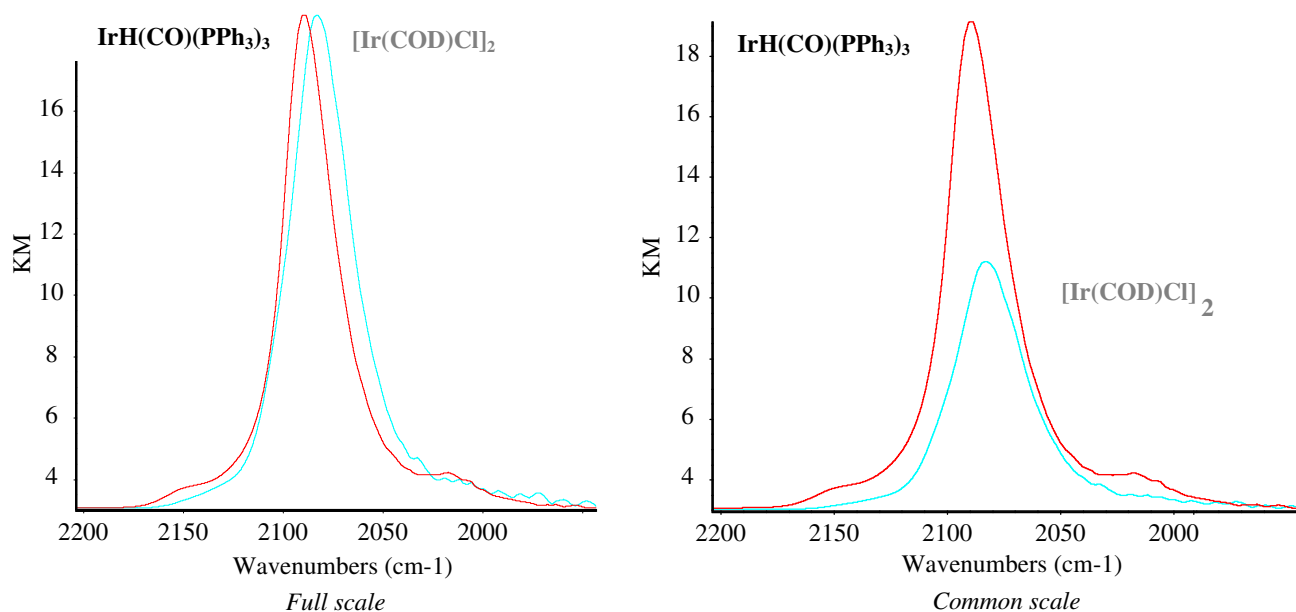
IrH(CO)(PPh₃)₃ [Ir(COD)Cl]₂

IrH(CO)(PPh₃)₃

[Ir(COD)Cl]₂

Full scale

Common scale

Fig. 10. IR spectra of the adsorption of CO by an active and an inactive catalyst.
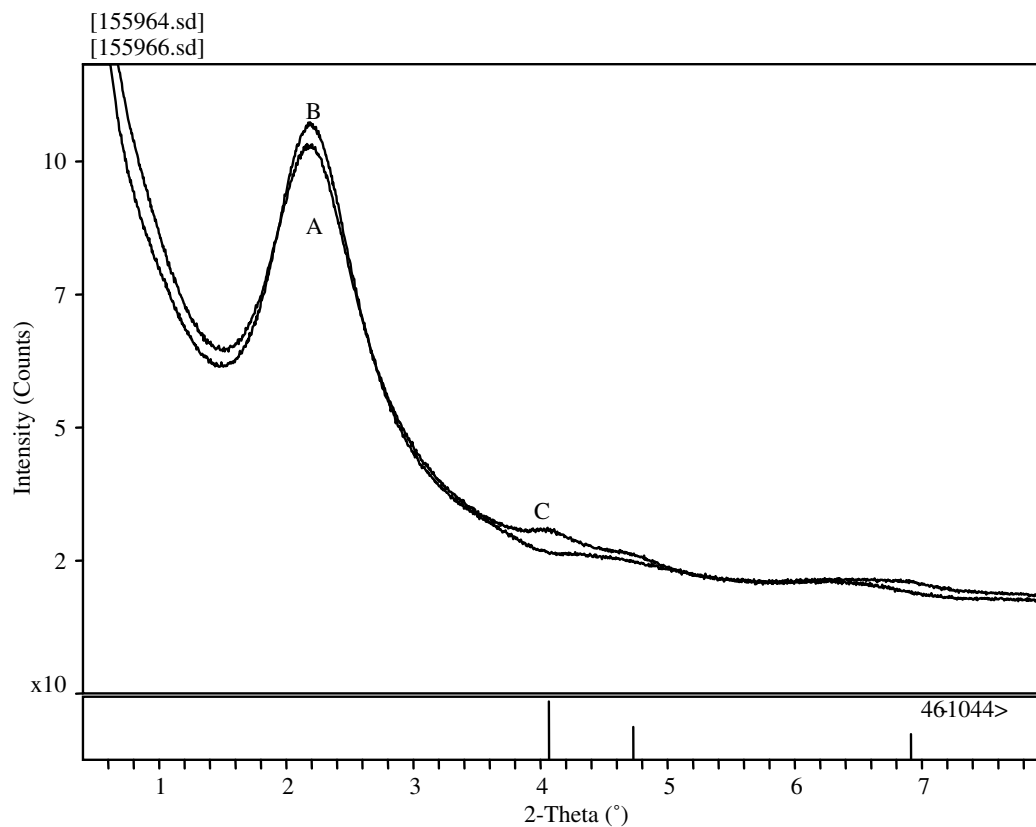
[155964.sd]
[155966.sd]

Fig. 11. X-ray diffraction pattern of catalyst no. **1** before (B) and after the run (A).

The X-ray diffraction pattern shows clear changes of the starting material. The three vertical lines at the bottom of the spectra indicate the diffraction pattern of iridium metal.[1] Before the experiment (B) there was no elevation of the base line in this region. After

the run there are vaults at all three positions of the metal indicating on iridium metal with a domain size of approximately 10–15 Å and amorphous silica (C).

Both X-ray diffraction patterns, before and after the experiment, look very similar. Changes in the big signal (A, B) can be caused by drying of the silica at elevated temperatures. The XRD indicated that no iridium metal is present. Because of the differences of these two patterns compared with those in Fig. 11 and of the similarities of the small vaults in the line (C) with the theoretical diffraction

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[1] A metal in this context is not defined by the oxidation state but by the particle size. If there is no metal in the XRD pattern, it means that there are no bigger conglomerates of metal clusters (>5 atoms) though it is possible to have a metal (0) in an extremely fine dispersed state.
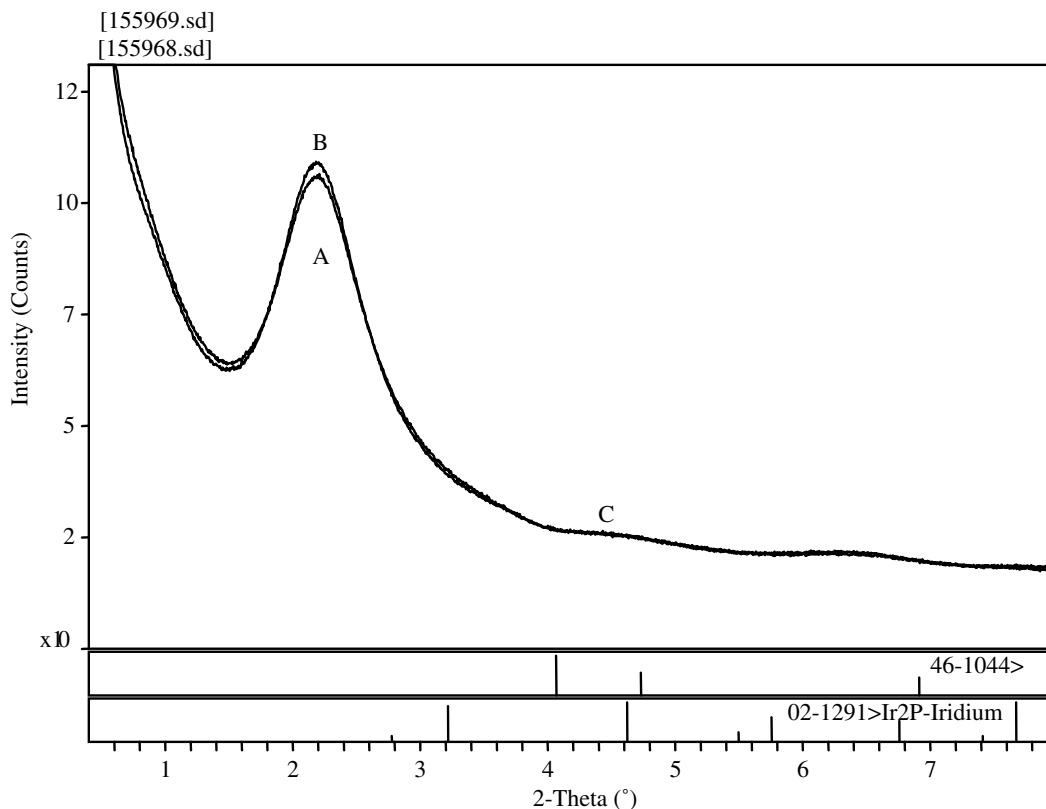
Fig. 12. X-ray diffraction pattern of catalyst no. **11** before (B) and after the run (A).

pattern of Ir₂P (see vertical lines at the bottom of the spectra), there is a strong suspect that an iridium phosphine compound is present. It has a domain size of less than 10 Å and exists along with amorphous silica (Fig. 12).

It can be summarized that the catalyst changes its composition during the experiments. The active species is not necessarily the original organometallic complex on silica. High activity requires phosphine ligands which can lose their aryl groups without losing their positive influence. The direct iridium–phosphorus interaction was proved by various analytical methods.

It is possible that the active species consists of extremely fine dispersed iridium(0) clusters or iridium phosphorus cages. Inactive species show bigger conglomerates of iridium atoms on the surface of silica.

4. Conclusions

Different heterogeneous catalysts were synthesized by using SiO_2 as support material and they were tested in thermal CH activation reactions (fixed bed reactor). The nature of the complex used for catalyst synthesis influenced the activity of the catalyst. A comparison of different iridium complexes (supported on SiO_2), led to conclusions about a remarkable correlation between the activity of the complexes and the number of their phosphine ligands. It became obvious that the activity of a catalyst system increases with a higher number of phosphane groups of the starting complex. For a more detailed investigation of this context, a certain amount of triphenylphosphine was added to less reactive catalysts (for example hexachloroiridic acid on silica, **1**) during their synthesis (ratios Ir:P = 1:4 or 1:8). Additionally functionalized silica containing phosphine groups was used for catalyst synthesis. Both methods gave rise to an enormous increase of activity. The conversion of isopentane to isopentene with catalyst **1** was improved by

the addition of triphenylphosphine from 0.8% to 29.4% (at 450 °C). The most important aspect is the fact that a "sacrificing olefin" is no longer necessary [17,18] to achieve such a performance.

Several analytical studies of the catalysts before and after the reaction allowed the exclusion of coking as the main reason for the deactivation of the systems below 500 °C. Additionally, the nature of the active species was investigated. It was proved that the catalyst undergoes decomposition at temperatures above 380 °C by loss of the phenyl groups stemming from triphenylphosphine. This has no negative impact on the activity. A consistent phosphorus content, even after the reaction, could be detected analytically.

Attempts to absorb carbon monoxide as well as XRD measurements indicated that the active species could be extremely fine dispersed iridium on amorphous silica, most likely associated with phosphorus, probably as iridium phosphide or as an iridium phosphorus cage or nanocluster. These conclusions are based on comparative measurements between active and low active catalysts before and after the dehydrogenation reaction. Low active catalysts showed bigger conglomerates of iridium metal, formed during the reaction which are obviously not able to activate CH bonds any more.

Acknowledgement

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