

A novel heterogeneous molecular catalyst for the Meerwein–Ponndorf–Verley and Oppenauer reactions

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Received 15 May 1996; accepted 9 June 1996

Abstract

The silica anchored mononuclear (tris)isopropoxyzirconium, $(\equiv\text{SiO})\text{Zr}(\text{O}i\text{-Pr})_3$, is an efficient catalyst for the reduction of ketones and the oxidation of alcohols by hydrogen transfer. Easy separation of the products and recyclability of the catalyst are demonstrated.

Keywords: Hydrogen transfer reduction; Silica supported zirconium catalysts; Alcohol oxidation; Ketone reduction

1. Introduction

The search for heterogeneous catalysts in the replacement of the homogeneous ones is dictated by economical, toxicological and/or ecological requirements. The so-called homogeneous supported catalysts have so far not found any application in an industrial process, although the knowledge of the surface chemistry involved in their synthesis has considerably improved during the last 15 years (for examples see [1]). The process of complex anchoring modifies the coordination sphere and/or the oxidation state of the metal, both being disastrous for the catalytic properties.

Our approach consists in chemically bonding molecular complexes to the surface of an inor-

ganic oxide so as to obtain well dispersed and isolated entities and then in modifying the coordination sphere around the metal center, in order to transform this surface complex into a site, catalytically active for the chosen target reaction. The solid is considered as a ligand, capable to intervene via electronic and/or steric effects; of course, this ligand must be stable under the catalytic conditions. We wish to report here the results of our first successful attempt using this approach. The catalyst is a mononuclear zirconium alkoxide, chemically bonded to the surface of a silica; the target reactions are the reduction of ketones and the oxidation of alcohols by hydrogen transfer, i.e. the so-called Meerwein–Ponndorf–Verley and Oppenauer reactions (MPVO). These reactions are known to occur in the presence of stoichiometric amounts of alkoxy complexes of alkali metals and aluminum [2,3]. More recently, alkoxides of group

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4 metals and lanthanides were shown to operate under catalytic conditions [4,5].

2. Experimental

Tetraneopentylzirconium, $ZrNp_4$, is prepared according to the procedure described by Lappert et al [6]. Silica (from Shell, 350 m²/g) is evacuated at 773 K (16 h, 10⁻⁴ Torr) prior to impregnation. Alcohols and ketones (from Aldrich, 98–99%) are used as received. The reaction is followed by GPC (Intersmat IGC 120), equipped with a Quadrex Q2 capillary column (0.32 nm, 15 m) and an FID detector.

The catalyst is prepared by impregnation of a pretreated silica (2 g) with a $ZrNp_4$ solution (200 mg, 5 ml) in *n*-hexane. After magnetic stirring of this slurry (298 K, 0.5 h), the solvent is removed via a canula and the solid is evacuated (10⁻⁴ Torr, 333 K, 10 h) in order to achieve complete reaction of the complex with silica and removal of traces of unreacted complex [7]. The solid is then contacted with 2-propanol (vapor pressure, 10 min) and then evacuated (298 K, 2 h). Three samples differing only slightly by their Zr content were prepared independently and tested for their catalytic properties: (1): 0.7 wt% Zr; (2): 0.8 wt% Zr; (3): 0.6 wt% Zr.

For the MPV reductions, a typical experiment is the following: The catalyst (100 mg, 7.6 10⁻⁶ mol Zr) is placed in a two-necked round bottomed flask equipped with a condenser and a rubber septum. After three cycles argon/vacuum, isopropanol (15 ml) and an internal standard are introduced via a syringe and then brought to reflux. Cyclohexanone (0.05 ml, 5 10⁻⁴ mol) in isopropanol (5 ml) is then added and the course of the reaction followed by GPC.

For the Oppenauer oxidations, the catalyst (100 mg, 7.6 10⁻⁶ mol Zr), then toluene (20 ml), an internal standard and the hydrogen acceptor (benzaldehyde (0.27, 2 10⁻⁴ mol)) are introduced in the flask as described above and the solution is brought to reflux. Cyclohexanol

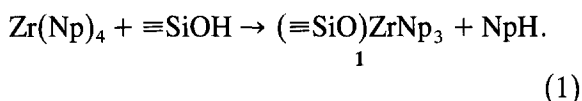
(0.056 ml, 5.45 10⁻⁴ mol) is then added and the reaction followed by GPC.

Analysis of the solution zirconium content is performed by ICP (Perkin Elmer) at the end of each experiment.

3. Results and discussion

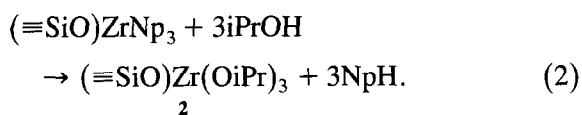
3.1. Synthesis of the catalyst

The reaction of tetraneopentylzirconium, $ZrNp_4$, with the surface hydroxyl groups of a silica, partially dehydroxylated at 773 K under vacuum, leads to the formation of the complex (siloxo)tris(neopentyl)zirconium, **1**, i.e. a mononuclear complex anchored to the surface of silica via a covalent bond between a surface oxygen atom and the metal (Eq. (1)) [7]:



The described pretreatment of silica ensures the obtainment mainly on the surface of the support of isolated hydroxyl groups [8] and thus, subsequently, the formation of the surface complexes **1** as well dispersed molecular species.

Controlled alcoholysis of **1** gives the surface alkoxycomplexes **2** (Eq. 2) as evidenced by evolution of neopentane:



Subsequent reaction of **2** with HCl/Et₂O liberates 3 ± 0.2 mol *i*PrOH/Zr, confirming the formulation of the catalyst. Moreover, we have checked that, under our conditions, $Zr(OiPr)_4$ is catalytically inactive; this confirms the stability of the $\equiv SiO-Zr$ bonds towards alcoholysis with *i*PrOH (Eq. (2)).

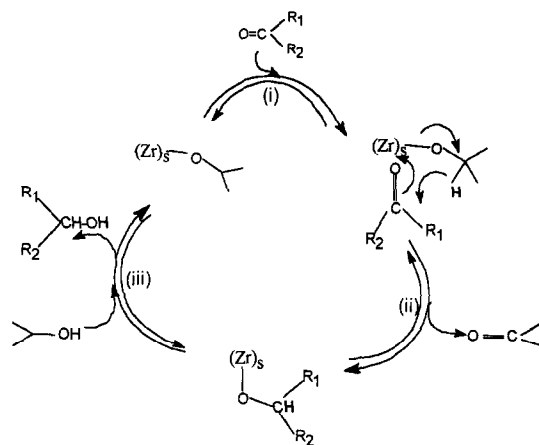
All the catalytic experiments are performed with this latter surface complex, obtained via alcoholysis with 2-propanol, which is the reductant we have chosen for the MPV catalytic reaction.

3.2. Catalytic properties of $(\equiv\text{SiO})\text{Zr}(\text{Oi-Pr})_3$ (2)

3.2.1. Catalytic properties for the reduction of ketones (MPV reaction)

When **2** is allowed to react in the presence of both a ketone and an alcohol, hydrogen transfer from the alcohol to the ketone occurs. Table 1 shows the results concerning the reduction of a number of ketones with 2-propanol (reductant and solvent) in the presence of the different samples of **2**.

Data of entries 1 and 3 attest to the reproducibility of the synthesis procedure of the catalyst. Most of the tested ketones are catalytically reduced. With none of them does one obtain side products, resulting from an aldol type condensation, followed or not followed by dehydration. This is attributed to the use of a large excess of 2-propanol, as previously observed [5]. Only the reduction of methyl phenylglyox-



Scheme 1.

Table 1
($\equiv\text{SiO})\text{Zr}(\text{Oi-Pr})_3$, catalyzed reduction of ketones with 2-propanol

entry	substrate	catalyst	conversion (%) ^a
1		1	66
		2	75
		1	52 ^b
		Zr(OiPr) ₄	0
2		1	28
3		3	38
		1	35
4		3	70 ^c
5		1	0
6		1	0
		2	0

^a After 20 h; (1) catalyst Zr: 0.7 wt%, [substrate]/[Zr] = 72; (2) catalyst Zr 0.8 wt%, [substrate]/[Zr] = 40; (3) catalyst Zr 0.6 wt%, [substrate]/[Zr] = 50.

^b Solvent: toluene; [2-propanol]/[cyclohexanone] = 5; $T = 393$ K; after 5 h of reaction.

^c Selectivity: 80% $\text{PhCH}(\text{OH})(\text{CO}_2\text{Me})$, 20% $\text{PhCH}(\text{OH})(\text{CO}_2\text{iPr})$.

ylate leads to a side reaction of significant importance (entry 4) i.e. transesterification of the initially formed methylmandelate to isopropyl mandelate (no isopropyl phenylglyoxylate was detected). Increasing the reaction temperature from 353 K to 383 K enhances significantly the reaction rate, by a factor of three with cyclohexanone for example (entry 1).




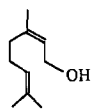
Among the unreactive substrates, one finds diphenylketone (entry 5) and 4-methyl-2-pentanone (entry 6). If one considers a catalytic cycle involving the following steps, [2] (i) coordination of the ketone to Zr, (ii) H transfer via a six-membered transition state, (iii) substitution of the alkoxy compound thus-formed by 2-propanol, (Scheme 1), then these observations can be explained either by steric effects (step i) or by unfavorable rates of the reaction of substitution of the alkoxy (from the ketone) by 2-propanol (step iii). With diphenylketone, steric effects are certainly predominant, inhibiting its coordination to Zr (presence of the bulky 'solid' siloxy ligand). This is confirmed by the following: if cyclohexanone is added after 20 h test time, the catalyst converts the latter with the same rate as a fresh catalyst. The behavior of 2-methyl-4-pentanone is not yet understood (entry 6). With acetophenone and 2,6-cyclohexanone (entries 2, 3) both steric and electronic effects certainly affect their reactivity.

No straightforward comparison can be made with zirconium based homogeneous catalysts [5], our working conditions being quite different (lower temperature, higher substrate/catalyst ratio). The supported zirconium catalyst **2** shows apparent lower activities; none of the tested ketones is totally converted as would be expected from thermodynamics [9]. Although the number of tested ketones is limited, the order of reactivity of the different ketones with our catalyst is very different from that reported by Ishii et al. [5], i.e. aromatic > alicyclic > aliphatic. This strongly suggests that the presence of the 'solid' siloxy ligand is an important parameter.

3.2.2. for the oxidation of alcohols (Oppenauer reaction)

The reverse reaction, oxidation of alcohols, is catalyzed by the same solid **2**. A preliminary test with cyclohexanol using acetone as oxidant (Table 2, entry 1) shows aldol condensation with formation of mesityloxide as the main

Table 2
(=SiO)Zr(OiPr)₃ catalyzed oxidation of alcohols with carbonyl compounds

entry	substrate	oxidant	catalyst	conversion (%) ^a
1		Me ₂ CO	2	trace
		PhCHO	1	40
		PhCOMe	2	49
2		PhCOMe	2	55 ^b
3		PhCHO	1	69
		PhCHO	1	48 ^c
4		PhCHO	1	46

(1) Catalyst Zr 0.7 wt%, [substrate]/[Zr] = 72; (2) catalyst Zr 0.8 wt%, [substrate]/[Zr] = 40; [oxidant]/[alcohol] = 5/1; solvent: toluene; *T* = 383 K unless specified otherwise.

^a After 6 h.

^b Solvent: octane.

^c *T* = 353 K.

product. Therefore, benzaldehyde and acetophenone were employed as oxidant in the following experiments (diphenylketone was discarded owing to its inactivity in the MPV reduction (Table 1, entry 5).






All tested alcohols are oxidized with moderate yields, but high selectivities (close to 100%) (Table 2). After 6 h, an equilibrium is reached in all cases except with phenylethanol, for which 24 h are needed. An increase of the temperature of reaction enhances the reaction rate, by a factor of two for the oxidation of phenylethanol by benzaldehyde for example and higher conversions are obtained (entry 3, Table 2). 4-Methyl-2-pentanol is oxidized by phenylacetone; remembering that 4-methyl-2-pentanone is not reduced by 2-propanol, this result suggests that the important step is the substitution of the alkoxy zirconium with the alcohol (step iii).

3.2.3. recyclability of the catalyst

The results obtained with the silica supported Zr complex **2** are very encouraging, although the reaction conditions are not yet optimized. We believe that they are nevertheless only interesting if the catalyst can be easily and efficiently recycled. After removal of the solution and washing of the solid with aliquots of solvent (20 ml *i*Pr-OH or toluene for MPV and O reactions, respectively) at the temperature of reaction until no reaction products can be detected in the solvent, a new solution of the reactants is introduced on the catalyst. The zirconium content of the successive catalytic solutions is analyzed. The results are summarized in Table 3.

Under MPV conditions (isopropanol as solvent, 353 K), all tests are satisfactory (entries 1–2, Table 3): very similar activities are observed for successive runs and no zirconium is detected in the liquid phase (the detection level corresponds to a loss of less than 1% of the introduced amount of Zr). Simultaneously, we have checked that, under our operating conditions, the complex tetraisopropoxyzirconium,

Table 3
Recycling tests of $(\equiv\text{SiO})\text{Zr}(\text{Oi-Pr})_3$ for the MPVO reactions

entry	substrate	catalyst	run n°	T (K)	conversion (%)
1		1	1	353	66 ^a
			2	353	67 ^a
			3	353	67 ^a
			4	383	55 ^b
2		3	1	353	38 ^a
			2	353	37 ^a
3		1 ^c	1	383	40 ^b
			2	383	32 ^b
4		1 ^c	1	383	77 ^b
			2	383	15 ^b
5		1 ^c	1	353	48 ^b
			2	353	15 ^b

^a After 24 h.

^b After 5 h.

^c Oxidant: benzaldehyde.

$\text{Zr}(\text{Oi-Pr})_4$, does not convert cyclohexanone; this strongly suggests that the complex remains grafted to the surface of silica and is the true catalyst (or catalyst precursor). Under Oppenauer conditions (entries 3–5, Table 3), the catalyst loses part of its activity already after the first run; the extent of this loss seems to be dependent on the substrate. With phenylethanol for example, the initial reaction rate is divided by a factor of ca. eight ($T = 383$ K). But no zirconium is detected in the liquid phase in the first run solution. One must then consider catalyst deactivation by formation of a stable intermediate. The following experiment confirms this hypothesis. Solid **2**, after catalysis with phenylethanol and benzaldehyde (run 2, Table 3) is treated with boiling 2-propanol and a new catalytic run is performed. Approximately 90% of the initial activity of **2** is restored. Deactivation of the surface complex may thus be attributed to the formation of a stable benzyloxylzirconium surface complex, which is not easily displaced by phenylethanol, but which can be substituted with isopropanol.

4. Conclusions

The complex, (siloxo)tris(isopropoxy)zirconium, which is chemically bonded to the surface of silica and obtained by a post-grafting modification of the coordination sphere of zirconium, is an heterogeneous molecular catalyst, designed for the reactions of hydrogen transfer between alcohols and ketones. This catalyst presents the advantage to be easily recycled after simple filtration and activation with boiling isopropanol. This suggests that during the catalytic cycle, the active species, $(\equiv\text{SiO})\text{Zr}(\text{Oi-Pr})_3$ is not transformed either in an inactive surface species (such as for example into small particles of zirconium oxide) or in a soluble complex; the $\equiv\text{SiO-Zr}$ bond is stable toward alcoholysis under MPVO conditions. Such stability may be related to the presence of the silicon atom, presenting empty d orbitals. [3] This same siloxy ligand may also be responsible of the differences observed for the order of reactivity as compared with homogeneous analogs. Studies are currently in progress to extend the domain of application of such catalytic solids, i.e. supported isolated active sites.

Acknowledgements

We are grateful to Dr. E. Poussen for fruitful discussions concerning the analysis of Zr by ICP. One of us (C.McG.) thanks the EEC for financial support through an Erasmus grant.

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