Chromium(VI) supported and entrapped on silica and zirconia as recyclable materials for oxidation of alcohols

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Abstract—Oxidation of alcohols have been realized with Cr(VI) oxide supported or entrapped, via sol–gel methodology, on silica and zirconia. These materials were easily recovered from the reaction mixture without leaching of chromium in solution. Moreover, recycling studies have indicated that they can be regenerated by calcinations at 400–600°C or by treatment with ozone at room temperature. In the case of Cr(VI) entrapped into silica matrix up to 18 oxidation cycles have been realized without loss in activity. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The oxidation of alcohols to aldehydes and ketones is a fundamental reaction in organic synthesis. A huge amount of different methods has been developed,[1] often using chromium(VI) reagents, such as, in addition to the *Jones' reagent*,[2] other dipyridine Cr(VI) oxide (Collins' reagent),[3] pyridinium chlorochromate (Corey's reagent),[4] pyridinium dichromate[5] and, more recently, 18-crown-6 complexes of *n*-butylammonium and pyridinium chlorochromates.[6] Some of these reagents are mild and selective oxidizing agents for alcohols but, must be used, at least, in stoichiometric amount. Moreover, the Cr^{6+} oxidant is usually not regenerated and the toxic effluents result in serious drawbacks. In order to overcome this problem the use of catalytic amounts of soluble chromium compounds in conjunction with more benign primary oxidants, such as *tert*-butyl-hydroperoxide (TBHP),[7] peroxyacetic acid[8] or hydrogen peroxide[9] has been developed. Our approach is based on the use of stoichiometric amounts of adsorbed or entrapped Cr(VI) on inert inorganic support that could be easily recovered and recycled. The concept of using reagents adsorbed on inert inorganic supports has been applied in organic synthesis. Such efficiency resulting from inorganic material-supported reagents may come from the combination of three factors: (i) an increase in the effective surface area for reactions; (ii) the presence of pores which constrain both substrate and catalyst and thus lowers the activation entropy of reactions; (iii) the acceleration of the reaction resulting from bringing substrate and reagent into proximity.[10] Literature data show that supported Cr ions are very reactive and readily interact with various organic and inorganic molecules.[11] These properties make such materials excellent catalysts not only for oxidation but also for hydrogenation-dehydrogenation and polymerization reactions. Chromium oxidants adsorbed on solid supports, such as chromic acid on silica,[12] chromyl chloride on silica/alumina,[13] pyridinium chlorochromate on alumina,[14] N-methyl piperidinium chlorochromate on alumina,[15] chromium trioxide on celite,[16] and on wet alumina[17] have been reported to give high yields under mild conditions. Chromium-substituted aluminophosphate-5 (CrAPO-5) was found to be an active and selective catalyst for the oxidation of secondary alcohols using either molecular oxygen or TBHP as the oxidant. However, the same authors later showed that the reaction occurred with chromium leaching from the catalyst.[18] In these cases no attempts to perform the recycling of these materials was realized. Indeed, since the chromium residues are environmentally hazardous it would be advantageous to develop oxidizing methods in which the chromium reagent can be easily recycled without any trouble in carrying out the work-up. Polymeric reagents, such as poly(vinylpyridinium dichromate),[19] poly(vinyl-pyridinium chlorochromate),[20] chromic acid on anion exchange resins[21] or imidazolium chlorochromate,[22] have been reported as recyclable oxidizing agents. However, the resins were regenerated after complete removal of the spent chromium salts. Probably one of the best recyclable oxidant is, in our opinion, Magtrieve™, based on chromium dioxide.[23]

In order to develop new recyclable materials for oxidation of alcohols we studied the behavior in the oxidation and recycling processes of Cr(VI) adsorbed on silica and zirconia. The results were compared with Cr(VI) entrapped
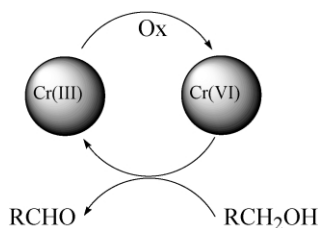
Figure 1. Oxidation cycles.

into silica[24] or zirconia matrix. The sol–gel technology offers several advantages over classical impregnation procedure employed in the preparation of heterogeneous catalysts. Purity, homogeneity and controlled porosity combined with the ability to form large surface area materials are the potential advantages of sol–gel processing.[25] Our investigation is based on some literature findings showing that Cr^{3+} species, formed on support after reduction, are reoxidable to Cr^{6+} to some extent[11] (Fig. 1).

2. Results and discussion

Four different oxidizing materials were used: adsorbed $Cr(VI)/SiO_2$ [adCr/SiO$_2$] and adsorbed $Cr(VI)/ZrO_2$ [adCr/ZrO$_2$] with a CrO_3 content of 4% wt; entrapped $Cr(VI)/SiO_2$ [sgCr/SiO$_2$] and entrapped $Cr(VI)/ZrO_2$ [sgCr/ZrO$_2$] with a metal loading of 4% and 9% wt, respectively. AdCr/SiO$_2$ and adCr/ZrO$_2$ were simply prepared by adding silica or zirconia to an aqueous solution of CrO_3 then evaporating to dryness. Sol–gel entrapped Cr/SiO_2 and Cr/ZrO_2 were prepared by using appropriate sol–gel procedures depending on the Si and Zr alkoxides reactivity.

2.1. Oxidation with adsorbed $Cr(VI)/SiO_2$ and adsorbed $Cr(VI)/ZrO_2$

The use of adCr/SiO$_2$ has been already reported by using diethyl ether as reaction medium.[12a] However, in this solvent we observed leaching of Cr in solution.[26] Other authors have found that a 3:1 ratio of dichloromethane: diethyl ether is optimal for oxidation of CrO_3 in presence of Celite.[16] In the present work the oxidation reactions have been carried out using as solvent dichloromethane or dichloromethane:diethyl ether 3:1. Interestingly, in these solvent systems no leaching of chromium was observed because of the incompatibility between solvent and Cr-species, as chromium trioxide is insoluble in dichloromethane. Indeed, oxidation of an alcohol with chromium trioxide does not take place when dichloromethane is employed. Using adCr/SiO$_2$ the reactions can be realized in these solvents. No difference was observed in yield or leaching of chromium in solution between dichloromethane: diethyl ether 3:1 and dichloromethane. In Tables 1 and 2 we report our oxidation data of several benzylic and aliphatic alcohols using adCr/SiO$_2$ and adCr/ZrO$_2$.

Oxidation of benzyl alcohols with adCr/SiO$_2$ gave quantitative yields in a 0.05 M solution. Primary alcohols such as 1-decanol gave a 90% conversion in a more diluted solution while 5-phenyl-1-pentanol needed a 4:1 Cr:alcohol molar

Table 1. Oxidation of alcohols with adCr/SiO$_2$

Entry	Compound	Aldehyde (conv.%)	M
1	$PhCH_2OH$	84	0.1
2	$PhCH_2OH$	99	0.075
3	$PhCH_2OH$	99	0.05
4	p-MeO-C$_6$H$_4$CH$_2$OH	99	0.05
5	p-Br-C$_6$H$_4$CH$_2$OH	99	0.05
6	$PhCHOHCH_3$	99	0.05
7	3-Thienyl-CH$_2$OH	99	0.05
8	$C_9H_{19}CH_2OH$	55	0.1
9	$C_9H_{19}CH_2OH$	85	0.05
10	$C_9H_{19}CH_2OH$	90	0.025
11[a]	$Ph(CH_2)_5OH$	89	0.025
12	Cyclohexanol	91	0.05
13	$C_8H_{17}CHOHCH_3$	89	0.025

SiO$_2$ Merck 0.063–0.200 mm. Reaction time 2 h. Molar ratio Cr/alcohol 2:1. Yields >99%.
[a] Molar ratio Cr/alcohol 4:1.

Table 2. Oxidation of alcohols with adCr/ZrO$_2$

Entry	Compound	Aldehyde (conv.%)	M
1	$PhCH_2OH$	97	0.1
2	$PhCH_2OH$	99	0.05
3[a]	$PhCH_2OH$	5	0.05
4	p-MeO-C$_6$H$_4$CH$_2$OH	98	0.05
5	$PhCHOHCH_3$	42	0.05
6	3-Thienyl-CH$_2$OH	76	0.05
7	$C_9H_{19}CH_2OH$	84	0.025
8[b]	$C_9H_{19}CH_2OH$	99	0.025

ZrO$_2$ calcined at 400°C for 4 h then 600°C for 2 h, 35 m^2/g. Reaction time 2 h. Molar ratio Cr/alcohol 2:1. Yields >99%.
[a] ZrO$_2$ calcined at 100°C overnight, 80 m^2/g.
[b] Molar ratio Cr/alcohol 4:1.

ratio to reach the same conversion. Secondary aliphatic alcohols gave similar conversions.

The use of adCr/ZrO$_2$ also gave good results. Benzyl alcohol can be oxidized quantitatively also in a more concentrated solution. Lower conversions were observed for 3-thienyl-methanol and 1-phenyl-ethanol (Table 2, entries 5, 6). Primary alcohol (1-decanol) was also quantitatively oxidized but using a 4:1 Cr/alcohol molar ratio (Table 2, entry 8). Chromium adsorbed on zirconia calcined at 100°C was not a useful oxidizing system (Table 2, entry 3).

2.2. Recycling studies with adCr/SiO$_2$ and adCr/ZrO$_2$

Since no leaching of chromium in solution was observed the complete recovery of the oxidizing system could be realized. The adsorbed or entrapped chromium species lead to a very easy work-up, which was reduced to a mere filtration. The spent adCr/SiO$_2$ reagent was washed with more dichloromethane, then dried in the oven for a few minutes. Regeneration of adCr/SiO$_2$ was realized by calcinations at 400°C for 1 h. After the first cycle we found a lower yield (87%). In the next cycles the yield decreased. Regeneration at higher temperature (600°C) gave large amount of α-Cr$_2$O$_3$ as detected by X-ray diffraction analysis.

These results could be ascribed to the fact that during calcination the supported chromium can anchor to the silica

support in an esterification reaction with the surface hydroxyl groups, yielding surface chromate(VI) species. Beyond a saturation coverage with such surface species, i.e. beyond a certain chromium content, which is determined by the nature of the support, excess of chromium species are converted to bulk α-Cr_2O_3 by calcinations at high temperature. With silica support, high chromium loading and calcination temperatures are believed to favor the formation of stable Cr_2O_3 crystallites. Diffuse reflectance UV-Vis spectroscopy and X-ray diffraction analysis showed in our case the presence of α-Cr_2O_3.[27] Indeed, since silica surface contains more acidic hydroxyl groups it has a poor capacity for Cr anchoring. As a result Cr_2O_3 particles are usually formed on silica surfaces, even at low Cr loading. On the other hand, for chromium loading of 1% wt, it has been reported that α-Cr_2O_3 is observed on zirconia only at the calcination temperature above 900°C, indicating that the zirconia support stabilizes supported chromium oxide with respect to silica support.[28]

Recycling of adCr/ZrO$_2$ was done at 600°C for 1.5 h. After the first regeneration the conversion was lower compared to adCr/SiO$_2$, however, it was constant in the next cycles differently from adCr/SiO$_2$ where the yield decreased in each cycle. In order to achieve higher conversions the reactions were also monitored for 24 h giving a 62–67% conversion. This remarkable lower conversion after the first regeneration could be related to the minor presence of hydroxy groups on the zirconia surface that allow the formation of chemically stabilized Cr^{6+} to a lesser extent.[29] Indeed, a model of supported chromium foresees a co-existence of chemically surface stabilized Cr^{6+} species with non-stabilized bulky Cr^{6+} species. The stabilized Cr^{6+} species are reduced to a lower oxidation state Cr species which are reoxidable whereas a part of the non-stabilized species can be transformed into α-Cr_2O_3 during calcinations. The rest is reduced, resulting in lower oxidation state Cr species which are not quantitatively reoxidable.[30] Comparing the results of cycles 2–6 for adCr/SiO$_2$ and adCr/ZrO$_2$ we can deduce that although a smaller portion of chromium on zirconia was stabilized, it appears to be more regenerate compared to the chromium on silica. Another aspect of the different behavior between these two systems could be related to the oxidation state of reduced Cr species on both supports. Several studies have been carried out in order to understand the oxidation state of supported chromium species. By treating at 120–600°C with a reducing agent, chromium oxidation state of +6 or +5 have been reported to be reduced mainly to Cr^{2+} and Cr^{3+} on silica and alumina surfaces, respectively.[31] On the other hand, Japanese authors claimed that Cr(VI) was reduced to Cr(IV) in the oxidation reaction of cyclohexanol at 110°C with chromium(VI) supported on ZrO$_2$, investigated by a temperature-programmed reduction method (TPR).[32]

However, it should be considered that results obtained by different groups are difficult to compare since the supported chromium may be present in a mixture of different valences and coordination environments, depending on the exact preparation.

Since conversions of regenerated adCr/ZrO$_2$ were not good we studied the oxidation of benzyl alcohol with adCr/ZrO$_2$

Table 3. Oxidation of benzyl alcohol (0.05 M) with adCr/SiO$_2$ and adCr/ZrO$_2$

	adCr/SiO$_2$		adCr/ZrO$_2$
# Cycles	Aldehyde (conv.%)[a]	Aldehyde (conv.%)[b]	Aldehyde (conv.%)[c]
1	99	99	99
2	87	99	55
3	86	99	56
4	80	99	55
5	63	97	54
6	58	86	54

Reaction time 2 h. Molar ratio Cr/alcohol 2:1. Cycles 2–6 correspond to five regeneration cycles.
[a] Regeneration of spent Cr(III) was done at 400°C for 1 h.
[b] Regeneration of spent Cr(III) was done at room temperature with O$_3$ for 24 h at 40 mA.
[c] Regeneration of spent Cr(III) was done at 600°C for 1.5 h.

using a 5.5:1 molar ratio Cr/alcohol in 0.02 M solutions (Table 4). The more diluted solutions were necessary in order to allow the regular stirring of the reaction mixtures. The oxidizing material was regenerated eleven times giving at last a constant conversion similar to that obtained with adCr/ZrO$_2$ used with a 2:1 Cr/alcohol molar ratio. Adsorbed Cr/SiO$_2$ was also regenerated at room temperature by packing the reagent in a column and letting the substrate stand in contact with a continuous ozone flow. After four regeneration cycles we found a lower yield (86%) in the last cycle (Table 3).

Regeneration by ozone is then more efficient since it retards the formation of α-Cr_2O_3 that is formed during the calcination procedure. Regeneration of adCr/ZrO$_2$ with ozone was not possible due to very small particles sizes that caused high pressure in the apparatus.

2.3. Oxidation with entrapped Cr/SiO$_2$ and entrapped Cr/ZrO$_2$ and recycling studies

The sol–gel entrapped sgCr/SiO$_2$ was prepared starting from chromium(III) chloride (see Section 4) to give a sol–gel entrapped Cr(III)/SiO$_2$. In order to have an oxidizing material, the sol–gel entrapped chromium(III) was oxidized to Cr(VI) by reaction with ozone. The Cr(VI)/SiO$_2$ reagent was obtained by packing the sol–gel Cr(III) in a column, letting the substrate stand in contact with a continuous ozone flow for several hours. At the end of the process the starting green silica turned to a red-brown material. Oxidation by heating in air at 550°C for 5 h was inefficient.

Table 4. Oxidation of benzyl alcohol (0.02 M) with adCr/ZrO$_2$

# Cycles	t (h)	Aldehyde (conv.%)	# Cycles	t (h)	Aldehyde (conv.%)
1	0.5	>99	7	3.5	82
2	3.5	95	8	3.5	68
3	3.5	87	9	3.5	69
4	3.5	79	10	3.5	53
5	3.5	82	11	3.5	53
6	3.5	76	12	3.5	53

Regeneration of spent Cr(III) was done at 600°C for 1.5 h. Molar ratio Cr/alcohol 5.5:1.

Table 5. Oxidation of benzyl alcohol with sgCr/SiO$_2$

# Cycles	t (h)	Aldehyde (conv.%)
1	48	98
2	48	98
3	48	98
4	23	>99
5	23	>99

Regeneration of spent Cr(III) was done at room temperature with O$_3$ for 48 h at 40 mA.

Oxidation of primary alcohols was carried out using a molar ratio Cr/alcohol of 2.5:1. No leaching of chromium in solution was observed. The spent sgCr/SiO$_2$ reagent was washed with more dichloromethane, then dried in the oven for a few minutes. Chromium(VI) was regenerated by packing the reagent in a column and again letting the substrate stand in contact with a continuous ozone flow as before. After several cycles, the sgCr/SiO$_2$ showed no change in the pore size distribution.

As reported in Table 5 excellent results were found. The oxidizing material was reused five times without loss in activity. In the first three cycles, the reaction time was longer, probably because the entrapped reduced chromium was oxidized with ozone for a shorter time (30 h). After these cycles the entrapped reduced chromium was oxidized for 48 h. Oxidation of sgCr(III)/ZrO$_2$ to Cr(VI) by calcination at 600°C for 1.5 h was successful. Using a molar ratio Cr/alcohol of 2.5:1 poor conversions were obtained (data not reported). Then this oxidizing system was used with a 5.5:1 molar ratio Cr/alcohol both at 0.02 M and 0.05 M. No difference was observed between these concentrations (Table 6). This ratio is calculated considering a metal loading of 9% wt [i.e. considering that the calcinations procedure gave a complete transformation of Cr(III) to Cr(VI)].

However, the poor conversions obtained with the 2.5:1 molar ratio induced us to carry out a TPR measurement in order to calculate the amount of Cr(VI) generated by calcination. This measurement showed that only ca. 15% of Cr(III) was oxidized.[27] This means that sgCr/ZrO$_2$ was actually used in about stoichiometric amount. In the first cycle the oxidation of benzyl alcohol was quantitative. This material was regenerated nine times giving high conversion ($\approx$90%) with the exception of the last reaction. Lower conversion was observed for the oxidation of 1-decanol in the first cycle. The good conversions obtained are a clear indication of the high recyclability of this material.

Table 6. Oxidation of benzyl alcohol (0.05 M) with sgCr/ZrO$_2$

# Cycles	t (h)	Aldehyde (conv.%)	# Cycles	t (h)	Aldehyde (conv.%)
1	22	>99	6	25	88
2	25	90	7	25	92
3^a	25	90	8	25	92
4	25	90	9	25	89
5	25	88	10	25	70
			1^b	24	45

Regeneration of spent Cr(III) was done at 600°C for 1.5 h.
^{a} 0.02 M.
^{b} 1-Decanol.

Table 7. Oxidation of benzyl alcohols with sgCr/SiO$_2$

# Cycles	Compound	t (h)	Aldehyde (conv.%)
6–7	p-Cl-C$_6$H$_4$CH$_2$OH	7	96
8–10	o-Br-C$_6$H$_4$CH$_2$OH	22	84
11–12	p-MeO-C$_6$H$_4$CH$_2$OH	5	>98
13–14	o-Me-C$_6$H$_4$CH$_2$OH	17	>98
15–16	o-EtO-C$_6$H$_4$CH$_2$OH	24	97
17^a	p-Cl-C$_6$H$_4$CH$_2$OH	24	38
18^b	C$_6$H$_5$CH$_2$OH	23	>99

Regeneration of spent Cr(III) was done at room temperature with O$_3$ for 48 h at 40 mA. Molar ratio Cr/alcohol 2.5:1. Solvent CH$_2$Cl$_2$/Et$_2$O 3:1.
^{a} Molar ratio Cr/alcohol 2:3.
^{b} Solvent CH$_2$Cl$_2$.

Finally, several benzylic alcohols were oxidized with sgCr/SiO$_2$ to the corresponding aldehydes in >99% selectivity and in 84–99% conversion in 5–24 h. The oxidation of benzylic alcohols reported in Table 7 were realized with sgCr/SiO$_2$ used five times for the oxidation of benzyl alcohol (Table 5). Then in Table 7 the number of cycles start from #6.

Both benzylic alcohols with electron-withdrawing or electron-donating groups were promptly oxidized.

3. Conclusions

In summary we have shown that chromium adsorbed or entrapped into silica or zirconia is a useful reagent for oxidation of alcohols. Moreover, since no leaching of chromium was observed before and after each reaction cycle it may be valuable in preventing environmental pollution. Cr(VI) oxide adsorbed on silica was better recycled by ozone while Cr(VI) oxide adsorbed or entrapped on zirconia gave high reproducibility in recycling process after the first calcination. Excellent results were obtained with the sol–gel entrapped Cr/SiO$_2$. The most interesting feature of this material was the recyclability (at least up to 18 times) without loss in activity.

4. Experimental

4.1. General

Diethyl ether was distilled under nitrogen from sodium benzophenone immediately prior to use. Dichloromethane was distilled under nitrogen from calcium hydride and used immediately. The reactions were monitored by GC–MS; all the products were identified and quantified by comparison with known samples. All the chemicals (Aldrich) used were analytically graded. Silica gel used was Merck (0.063–0.2 mm; 450 m^2/g).

4.1.1. Preparation of adCr/SiO$_2$ and adCr/ZrO$_2$. In a 100 mL round-bottom flask were dissolved 400 mg of CrO$_3$ in 30 mL of distilled water, then SiO$_2$ or ZrO$_2$ (10 g) was added. The mixture was stirred, evaporated under reduced pressure to dryness, then left in the oven at 80°C overnight.

The zirconia sample was prepared by hydrolysis and poly-condensation of zirconium n-propoxide Zr(OCH$_2$CH$_2$CH$_3$)$_4$

in *n*-propyl alcohol, according to a published procedure.[33] The hydrolysis was carried out by an abrupt addition of aqueous solution (in excess with respect to the stoichiometric ratio) to zirconium precursor. The reactants and the relative amount in a typical preparation are the following: $Zr(OCH_2CH_2CH_3)_4$ (40 g) was added to *n*-propyl alcohol/H_2O (1:1, 100 mL). The white precipitate was refluxed at 100°C overnight, then was filtered and washed with bi-distilled water. After drying at 100°C for 12 h, the solid was ground and calcined in air in two steps: at 400°C for 1 h, then at 600°C for 2 h. According to the literature,[33] the crystallization products of amorphous zirconia contain along with the monoclinic also the metastable tetragonal phase. The sample has surface area of 35 m^2/g (as determined by nitrogen adsorption/desorption measurements at 77 K) and a mean pore size distribution of 30 Å.

4.1.2. Preparation of sgCr/SiO$_2$. Tetraethoxysilane (20.83 g, 0.1 mol) was added to an aqueous solution of HCl (0.01N, 10 mL) and mixed with ethanol (5 mL) as co-solvent. The mixture was stirred for 30 min to obtain a sol containing principally hydrolyzed tetraethoxysilane. In order to complete the hydrolysis step, the ethanol was removed by distillation under vacuum at 35°C. Next, the sol solution was cooled at 0°C to avoid gelation that would be promoted at room temperature. Chromium(III) chloride hexahydrate (2.66 g, 0.01 mol) was dissolved in 10 mL of bi-distilled water and cooled at 0°C. Finally, the solution containing chromium chloride was added slowly to the sol and the pH was raised from 2 to 4.

The gelation occurred in about 20 h. The resulting oxide ground in granules (<425 μm) was washed with water and sonicated for 30 min in the same solvent in order to remove any chromium compound that adhered onto the outer surface of the silica matrix. The resulting material was heated to 70°C until a constant weight was achieved (24 h). The Cr(III) in the washing solution was determined spectrophotometrically as CrO_4^{2-}. The calculated content of the silica entrapped chromium was of 4% wt. Before use the resulting oxide was dried at 25°C at 1 mmHg for 12 h.

The sgCr(III)/SiO$_2$ (3.217 g) was placed in a column and a continuous ozone flow (10 Nl/h, ca. 50 mg O_3/h) was allowed to pass through for 31 h. At the end of the process the starting green silica turned to a red-brown material.

The sample showed a very high surface area (650 m^2/g) with a pore size distribution centered at 10–20 Å as determined by nitrogen adsorption/desorption measurements at 77 K. The X-ray diffraction pattern showed only the background of the silica amorphous glass. No reflections due to any chromium oxide phase were detected.

4.1.3. Preparation of sgCr/ZrO$_2$. The sol–gel entrapped Cr/ZrO$_2$ was synthesized by hydrolytic polycondensation of zirconium *n*-propoxide $Zr(OCH_2CH_2CH_3)_4$, using $CrCl_3 \cdot 6H_2O$ as chromium precursor. In a typical preparation, $CrCl_3 \cdot 6H_2O$ (8 g, 0.03 mol) was dissolved in 20 mL of bi-distilled water, then the resulting solution was added at room temperature to a well-stirred solution of the zirconium *n*-propoxide (40 g, 0.12 mol) in *n*-propyl alcohol. After the addition of chromium solution, a fine precipitate immediately was formed and the suspension was refluxed at 100°C

overnight. The resulting solid was filtered, washed with bi-distilled water and dried at 100°C for 20 h. The Cr(III) in the washing solution was determined spectrophotometrically as CrO_4^{2-}. The calculated content of entrapped chromium was 9 wt%. In order to have an oxidizing material, the sol–gel entrapped Cr(III) was oxidized to Cr(VI) by successive calcination in air at 400°C for 2 h, then at 600°C for 1.5 h. During the calcination process, crystallization of zirconia from amorphous to tetragonal phase occurs. No diffraction lines of the monoclinic form were detected. The sample showed a surface area of 40 m^2/g with a pore size distribution centered at 20 Å as determined by nitrogen adsorption/desorption measurements at 77 K.

4.1.4. General procedure for oxidation reactions. In a typical procedure with adCr/SiO$_2$ a round-bottom flask was filled with Cr(VI)-reagent (1.00 g), dichloromethane or dichloromethane/diethyl ether 3:1 (0.05 or 0.02 M) and the alcohol (21.6 mg) under argon. The reactions were carried out at 25°C with magnetic stirring. At the end the reaction mixture was filtered, washed with 5 mL of ethyl acetate. The Cr(VI)-reagent was dried in the oven (80°C) for 1 h, then regenerated.

4.1.5. General procedure for regeneration by calcination. Adsorbed and entrapped Cr(VI) samples were regenerated by calcination in air, in dynamic conditions, by increasing the temperature from room temperature to 400–600°C (heating rate 10°C/min). Usually, 2 g of spent sample was put in a ceramic dish and calcined up to 400°C for 1 h, in the case of adCr/SiO$_2$, and up to 600°C 2 h for adsorbed and sol–gel Cr/ZrO$_2$.

4.1.6. General procedure for regeneration with ozone. Adsorbed or entrapped Cr/SiO$_2$ was regenerated at room temperature by packing the reagent in a column and letting the substrate stand in contact with a continuous ozone flow, usually 50 mg/h within 48 h at 40 mA.

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