Solvent-free oxidation reactions with Ti-MCM-41 and TS-1 catalysts occluded in polydimethylsiloxane (PDMS) membranes

Ivo Vankelecom,*† Karen Vercruysse, Nancy Moens, Rudy Parton, Jale Sudhakar Reddy and Pierre Jacobs

Centre for Surface Chemistry and Catalysis, Faculty of Agricultural and Applied Biological Sciences, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, 3001 Leuven, Belgium

The incorporation of TS-1 and Ti-MCM-41 catalysts in PDMS is proven to enable the oxidation of hexane and epoxidation of *cis*-cyclooctene, respectively, with high conversions under solvent-free reaction conditions.

In 1994,[1] we reported a new type of catalytically active membrane, consisting of a FePcY zeolite (ironphthalocyanine occluded in zeolite Y) that was dispersed in a polymeric phase (PDMS). This catalytic system enabled the oxidation of cyclohexane under solvent-free conditions in a counter-current membrane configuration. Furthermore, the new hydrophobic environment of the catalyst created by this PDMS membrane acted as a 'solvent phase' and led to strongly increased conversions.[1–3] Here, we describe two new examples of successful incorporation of oxidation catalysts in PDMS: mesoporous Ti-MCM-41[4] and microporous TS-1,[5] both Ti-containing structures. They are used in the epoxidation of *cis*-cyclooctene and in the oxidation of hexane respectively. A set of reactions have been carried out to demonstrate the influence of the hydrophobic PDMS membrane on the activity of these catalysts with or without any solvent.

Ti-MCM-41 and TS-1 were synthesised following known procedures.[4,6] In the synthesis of Ti-MCM-41 (Ti/Si = 52), 18.8 g Ludox AS-40 (40 mass% colloidal silica in water, Dupont) were mixed with 19.4 g tetraethylammonium hydroxide (TMAOH, 20 mass% in water, Fluka) and 16.1 g cetyltrimetylammonium chloride (CTMACl, 25 mass% in water, Aldrich). After stirring for 15 min, a second portion (32.2 g) of CTMACl was added followed by 3.64 g $Ti(OBu^n)_4$ (99%, Alfa) dissolved in 3.60 g of isopropyl alcohol (99.5%, Aldrich). The complete synthesis was performed in ice-cooled glass containers. After homogenization, the synthesis gel was poured into stainless-steel autoclaves which were placed in a rotating oven at 383 K for 24 h. After synthesis, the autoclaves were cooled and the catalyst was filtered, washed several times, and dried at 333 K over 10 h.

TS-1 (Ti/Si = 50) was prepared by stirring 1.94 g $Si(OEt)_4$ (98%, Aldrich), 0.20 g $Ti(OEt)_4$ (99%, Aldrich) and 20.3 g tetrapropylammonium hydroxide (40 mass% aqueous solution, Fluka) at 330 K under a nitrogen atmosphere over 3 h. The resulting clear solution was poured into a Teflon-lined stainless-steel autoclave which was placed in an oven at 450 K for 24 h. The catalyst was separated by centrifugation and washed several times with deionised water before it was dried at 333 K over 10 h. Both TS-1 and Ti-MCM-41 were calcined at 820 K over 12 h, using a heating rate of 1 K min^{-1}.

Before using the TS-1 and Ti-MCM-41 catalysts, they were thoroughly characterised by chemical analysis, XRD, IR and UV–VIS DRS. These characterization techniques indicated that these materials possessed properties similar to those reported in the literature. In the case of Ti-MCM-41, the peaks on the XRD pattern could be indexed on a hexagonal lattice with a pore diameter of 38 Å. Raman and UV–VIS revealed the absence of anatase impurities.

The earlier described method[7] to prepare zeolite-filled membranes could no longer be applied here as the PDMS prepolymer would completely obstruct the mesopores of Ti-MCM-41 during the membrane synthesis. Therefore, a new preparation method, developed by Vankelecom *et al.*,[8] was used in which a partially polymerised network is formed before the catalyst is added. PDMS-prepolymer and crosslinker (General Electric, RTV-615A and B respectively) were mixed in a 10 : 1 ratio. For Ti-MCM-41 containing membranes, a 20 mass% mixture of PDMS in 4-methylpentan-2-one (99.5%, Acros Chimica) was prepolymerised over 1 h at 343 K. When incorporating TS-1, a 15 mass% mixture of PDMS in 4-methylpentan-2-one was stirred at 328 K for 1.5 h. The catalyst was added in a 13 mass% (relative to PDMS) loading in the case of Ti-MCM-41 and in a 17 mass% loading for TS-1. After thorough mixing at room temperature, the suspension was poured into a Petri dish and the solvent was allowed to evaporate overnight. The final curing of the polymer took place in a vacuum oven at 423 K over 1 h. TS-1 and Ti-MCM-41 catalysts embedded in PDMS are denoted as TS-1/PDMS and Ti-MCM-41/PDMS, respectively. *n*-Hexane (10 g) was oxidised in a 100 ml capacity Parr reactor at 373 K using 25 g of a 35 mass% hydrogen peroxide (Acros Chimica) solution in water with 0.25 g TS-1. If a solvent was used in the reaction, 38 g was added to 5 g of hexane, 12 g of hydrogen peroxide and 0.25 g of TS-1. Heptane was used as external standard in the GC analysis of these reactions.

The epoxidation of *cis*-cyclooctene (95%, Aldrich) over Ti-MCM-41 was performed at 330 K in a round-bottomed flask with condensor. 8 g of substrate were reacted with 8.4 g of *tert*-butyl hydroperoxide (70 mass% aqueous solution, Acros Chimica) over 0.2 g of dry Ti-MCM-41. Chlorobenzene (99%, Acros Chimica) was used as external standard for quantitative GC analysis.

The results obtained in the oxidation of *n*-hexane are summarised in Table 1. Under solvent-free reaction conditions,

Table 1 Oxidation of *n*-hexane with hydrogen peroxide over TS-1 at 373 K

	No solvent[a]		Methanol[b]	
	TS-1	TS-1/PDMS	TS-1	TS-1/PDMS
TON[c]	280	870	520	440
Product distribution (%)				
Alcohols	5	9	22	30
Ketones	50	51	70	62
Acids	38	38	4	6
Other[d]	7	3	4	3
Peroxide efficiency (%)[e]	26	80	65	59
Peroxide conversion (%)[f]	99	99	99	92

[a] *Reaction conditions*: TS-1 = 0.25 g; substrate = 10 g; H_2O_2 (35 mass% in water) = 25 g. [b] *Reaction conditions*: TS-1 = 0.25 g; substrate = 5 g; H_2O_2 (35 mass% in water) = 12 g; methanol = 36 g. [c] TON (turnover numbers) after 5 h reaction. [d] Mainly methyl ethers (when using methanol as solvent) and polyfunctional compounds. [e] Peroxide efficiency = 100 × (mmol peroxide utilized in product formation/mmol peroxide consumed). [f] Peroxide conversion = 100 × (mmol peroxide consumed/mmol peroxide at the end of the reaction). The remaining H_2O_2 was estimated by titration using a 0.1 m $Ce(SO_4)_2$ solution.

the positive role of the membrane is obvious: the TON (turnover number) is only 280 over TS-1 as compared to 870 over the TS-1/PDMS catalyst. The major products are hexan-2-ol, hexan-3-ol, hexan-2-one and hexan-3-one. By-products, mainly acids, are formed by consecutive oxidation reactions. The very high activity obtained over the membrane-occluded catalyst can be ascribed to the combination of two beneficial effects: (*i*) the hydrophobic nature of the PDMS membrane concentrates the non-polar *n*-hexane around the catalyst particle and (*ii*) the density of the composite membrane makes the incorporated catalyst reside at the interface of both reagent faces, whereas the non-embedded catalyst mainly resides in the aqueous phase at the bottom of the reactor. The conversion of hydrogen peroxide is almost complete in all cases.

When methanol is added as a solvent under comparable conditions, the catalyst powder performs better than the TS-1/PDMS. However, the TON is about halved as compared with TS-1/PDMS under solvent-free conditions. Clearly, the solvent causes a dilution of the reagents. On the other hand, the presence of methanol molecules in the zeolite pores reduces the secondary oxidation reactions by enhancing the removal of the reaction products out of the zeolite pores. Under solvent-free reaction conditions, the residence time of the primary oxidation products in the zeolite pores is higher.

The advantage of a PDMS membrane is further evidenced in the epoxidation of *cis*-cyclooctene with Ti-MCM-41. After only 7 h, 50% of the theoretical maximum conversion is reached, whereas only 8% is converted with the non-membrane resident catalyst a value which hardly exceeds the conversion in a blank reaction.

Table 2 Epoxidation of *cis* cyclooctene with *tert*-butyl hydroperoxide over Ti-MCM-41 at 330 K[a]

	Theoretical conversion (%)[b]		Epoxide selectivity (%)[c]		Peroxide efficiency (%)[d]	
t/h	7	24	7	24	7	24
No catalyst	—[e]	10	—[e]	81	—[e]	90
Ti-MCM-41	8	14	82	81	95	95
Ti-MCM-41/PDMS	50	72	70	75	97	95

[a] *Reaction conditions*: Ti-MCM-41 = 0.2 g; substrate = 8.4 g; *tert*-BHP (70 mass% in water) = 4 g. [b] Conversion (%) = 100 × (mmol products formed/mmol *tert*-BHP initially present). [c] Epoxide selectivity (%) = 100 × (mmol epoxide/mmol total products). [d] Per- oxide efficiency (%) = 100 × (mmol *tert*-BHP used in product formation/mmol *tert*-BHP consumed). [e] Not determined.

With these two examples, we have proved the versatility of our earlier reported membrane-occluded catalyst system (FePcY–PDMS). The results confirm that a membrane resident catalyst is able to create an excellent activity under biphasic reaction conditions. However, consecutive oxidation reactions might assume significance as a possible drawback in the absence of a solvent. The application of catalytic membranes in a counter-current membrane reactor might not only reduce this problem, but will most probably further improve the performance of membrane-resident catalysts.

We are grateful to the Belgian Government for the support in the frame of a IUAP-PAI grant on supramolecular Catalysis. R. P. and I. V. thank the Belgian National Fund of Scientific Research (N. F. W. O.) for grants as Post-Doctoral Researchers.

Footnote

† E.mail: ivo.vankelecom@agr.kuleuven.ac.be

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Received, 8th October 1996; Com. 6/06907J