ELSEVIER

Catalysis Today 61 (2000) 29–36

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Supported micelles in biphasic oxidation catalysis

S.C. Tsang*, N. Zhang, L. Fellas, A.M. Steele

Catalysis Research Centre, Department of Chemistry, The University of Reading,
Whiteknights, Reading RG6 6AD, UK

Abstract

The research is concerned with a novel way of heterogenising a simple water-soluble salt, ammonium molybdate for catalytic cyclohexene oxidation with *tert*-butyl hydroperoxide (TBHP) in bulk dichoromethane. Surface tethered surfactant molecules created were presumed to form supported micellar assemblies. These assemblies carried microscopic water droplets in turn containing the ammonium molybdate catalyst for use in a biphasic oxidation reaction. Thus heterogenisation of the water-soluble molybdate was accomplished through water droplet immobilisation but without anchoring the catalytic component directly. Our results clearly showed that a faster oxidation rate was obtained using the silica supported with surfactant molecules than with the corresponding supported aqueous catalyst on unmodified silica. This implied that the oxidation catalysis occurred within the small surface supported surfactant assemblies as 'nano-reactors', whose controlled hydrophobic and hydrophilic affinities in this microenvironment significantly improved the mass transfer efficiency of reaction components. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Nano-reactor; Supported aqueous phase catalysts; Biphasic; Epoxidation

---

1. Introduction

Homogeneous catalysts frequently display superior activity and selectivity compared with their heterogeneous counterparts. The traditional approach of immobilising active homogeneous species onto solid supports in order to facilitate separation is largely unsuccessful on a technological scale (loss in activity and selectivity, catalyst leaching). In contrast, an alternative approach of using a biphasic system, which is being realised industrially, represents a technological breakthrough. The concept depends on the use of two immisible liquid phases, such that the homogeneous catalyst is soluble in one phase (e.g. water) and the product in the other phase (organic). The product can then be obtained by a simple phase separation. Industrial applications have been quickly established, such as, the Ruhrchemie AG/Rhône-Poulenc process for the hydroformylation of propylene [1]. However, the major problems of this present technology which limit wider applications are the *intrinsic low solubility of organic reactants in water* in which the catalyst resides, *a limited interface between the reactants* and *some catalyst loss* between the immisible liquids [1].

---

* Corresponding author. Tel.: +44-118-9316346;
fax: +44-118-9316632.
E-mail address: s.c.e.tsang@reading.ac.uk (S.C. Tsang).

PII: S0920-5861(00)00360-6

Recent interest has focussed on creating a thin water film on a high surface area support surrounded by a bulk organic solvent, the so-called supported aqueous phase catalyst (SAPC). SAPC substantially increase the interfacial surface area and provide an elegant way of heterogenizing biphasic catalysts [2–5]. The molecular catalyst dissolving in water is then immobilised without any chemical attachment via an ultrathin water film. This is physically supported on a selected surface with the organic phase containing reactants and products. These SAP catalysts have been successfully tested for reactions such as hydroformylation of heavy or functionalized olefins, selective hydrogenation of α,β-unsaturated aldehydes, and asymmetric hydrogenation [4,5]. Their main advantages concern easy catalyst recovery and increased activity. However, this system still suffers from mass transfer problems despite the sharp increase in interfacial surface area and the leaching problems of the expensive water-soluble organometallic catalysts developed for the described reactions.

Oxidation is arguably the most important industrial catalytic reaction. It is therefore not surprising that a large number of catalytic systems have been described for this type of reaction. Most catalytic oxidations in the liquid phase involve the use of homogeneous catalysts and it is well known that many simple water-soluble metal salts show a high activity in the presence of an oxidant [8]. In some cases, e.g. in terephthalic acid production by catalytic oxidation of *p*-xylene in acetic acid, this is not a problem as the product crystallizes out and the catalyst-containing liquors are recycled. In many cases, however, expensive and cumbersome steps will be involved to separate reaction components from catalysts after oxidation reactions. There is therefore a major advantage of using a heterogeneous oxidation catalyst [6]. However, it is evident from the literature that the only truly commercial heterogeneous catalysts are titanium(IV) silicalites (TS-1) (developed by Enichem workers) with a minor problem of metal leaching, as other generally expensive immobilised redox catalysts suffer from severe leaching problems. On the other hand, there are many simple and inexpensive water-soluble transition-metal salts with excellent activity and selectivity only if they can be heterogenised onto a high surface area support. Hence, even if some slow catalyst leaching occurs this may not create insurmountable problems.

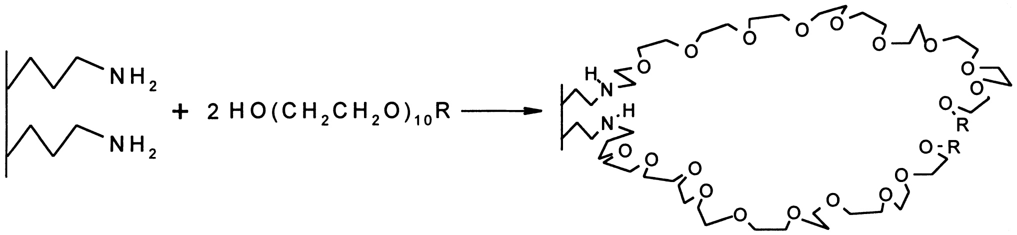
Here we report for the first time, the application of the SAP methodology to perform liquid phase cyclohexene oxidations using a simple water-soluble ammonium molybdate catalyst with the aid of the supported surfactants. It is envisaged that the anchored surfactant molecules could form micellar aggregates on the surface. The micelles may support small water droplets that in turn carry the molybdate catalyst. Thus, the supported surfactant assemblies are believed to improve the interactions between hydrophilic and hydrophobic species due to the particular microenvironment and also serve to separate the reaction components.

2. Experimental

2.1. Preparation of silica tethered with surfactant molecules

Ultra high pore volume (UHPV) silica (**A**) was obtained from Aldrich Chemicals. The silica was heated from room temperature to 150°C and held for 2 h under a dynamic vacuum (1×10^{-2} Torr) prior to use. 4.0 g of the silica was allowed to react with 7.0 cm^3 of 3-aminopropytriethoxysilane (APTES, >99%, BDH) in refluxing dry toluene (50 cm^3) under an argon atmosphere for 12 h. After reaction, the mixture was filtered, washed with dichloromethane, transferred to a Soxhlet thimble and exhaustively washed to remove any excess of the APTES. The washing was effected with 1:1 solution of dichloromethane and diethylether vapour condensate under refluxing conditions and flowing argon gas for 12 h. After the mixture was filtered and dried this yielded solid product **B**. The solid product **B** was then allowed to react with 15.0 g polyoxyethylene stearyl ether surfactant ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$, Aldrich) in refluxing toluene (200 cm^3) for 12 h under an argon atmosphere. The residue was collected from filtration, washed with dichloromethane and Soxhlet washed with dichloromethane–ether mixture and air-dried at 90°C. This yielded product **C**. A similar procedure was followed for the preparation of SAP on MCM41.

The following reaction was expected:



(B) **(C)**

2.2. *Preparation of supported aqueous phase (SAP) on unmodified silica and surfactant-tethered silica*

Hydrated ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) of 0.618 g was mixed with 3.0 cm^3 D.I. water and 0.5 g of unmodified silica (**A**) or the surfactant tethered silica (**C**). The mixture was then stirred overnight. Excess water was pumped off under a dynamic vacuum (1×10^{-2} Torr) at room temperature for 1 h and then at 60°C for another 1 h.

2.3. *Catalysis*

SAP catalyst of 0.2 g prepared as described and a magnetic stirrer was added to a 100 cm^3 three neck round bottom flask fitted with a thermometer, reflux condenser and a tapped dropping funnel. The apparatus was flushed with argon for 30 min before the addition of 10.0 cm^3 dichloromethane, 1.26 cm^3 pure cyclohexene (>99%, Sigma), 1.0 cm^3 *tert*-butylhydrogenperoxide (TBHP, 5.5 M in *n*-decane) via the dropping funnel where 2:1 molar ratio of cyclohexene to TBHP is maintained. The mixture was then refluxed with continual stirring at about 45°C for 24 h. The mixture was then allowed to cool, the supernatent was collected and centrifuged (4000 rpm, 4 min) and analysed.

3. Results and discussions

3.1. *Silica tethered with surfactant molecules*

The initial methodology of APTES immobilisation onto silica surface was achieved according to a modified method published by Sutra and Brunel [7] who attached 3-chlorotripropylsilane ($(PrO)_3Si$–) onto the internal surface of mesoporous MCM41 silica via propanol elimination to forming Si–O–Si bonds. In this case, EtOH elimination would be expected through the APTES attachment on silica. FTIR spectra of silica before and after modification (reacted with APTES and surfactant molecules, exhaustively washed in dichloromethane–ether and dried; **A** vs. **C**) clearly shows new absorption peaks at (2922.5, 860.0 and 698.6 cm^{-1}). These peaks can be undoubtedly attributed to the C–H stretching and bending modes associated with organic molecules. No such peaks were detected when the silica was immersed initially with APTES and surfactant mixtures at room temperature, filtered and then Soxholet washed with dichloromethane–ether under identical treatments. This suggested that the silica surface had been chemically tethered with organic groups rather than physical retention of the organic compounds inside the porous structures. The TG and DTA curves of pure silica in Fig. 1a indicated a significant endothermic weight loss (5%) at around 100°C and a gradual weight loss (further 2.3%) from 100 to 800°C attributed to the removal of physisorbed water and surface dehydroxylation, respectively. In the case of the surfactant modified silica (**C**) (Fig. 1b), it displayed two extra exothermic events at 330 and 550°C accounting for a greater weight loss (about 8 %) from 100 to 800°C. This was assigned to the combustion of surface organic groups when the sample was heated in air. However, no further analysis was attempted to differentiate the two exothermic peaks. We believe that the reaction of supported APTES with surfactants would occur favourably by using excess surfactant molecules in *dry* refluxing organic solvent, which would drive the reaction forward resulting in the surfactant attach-

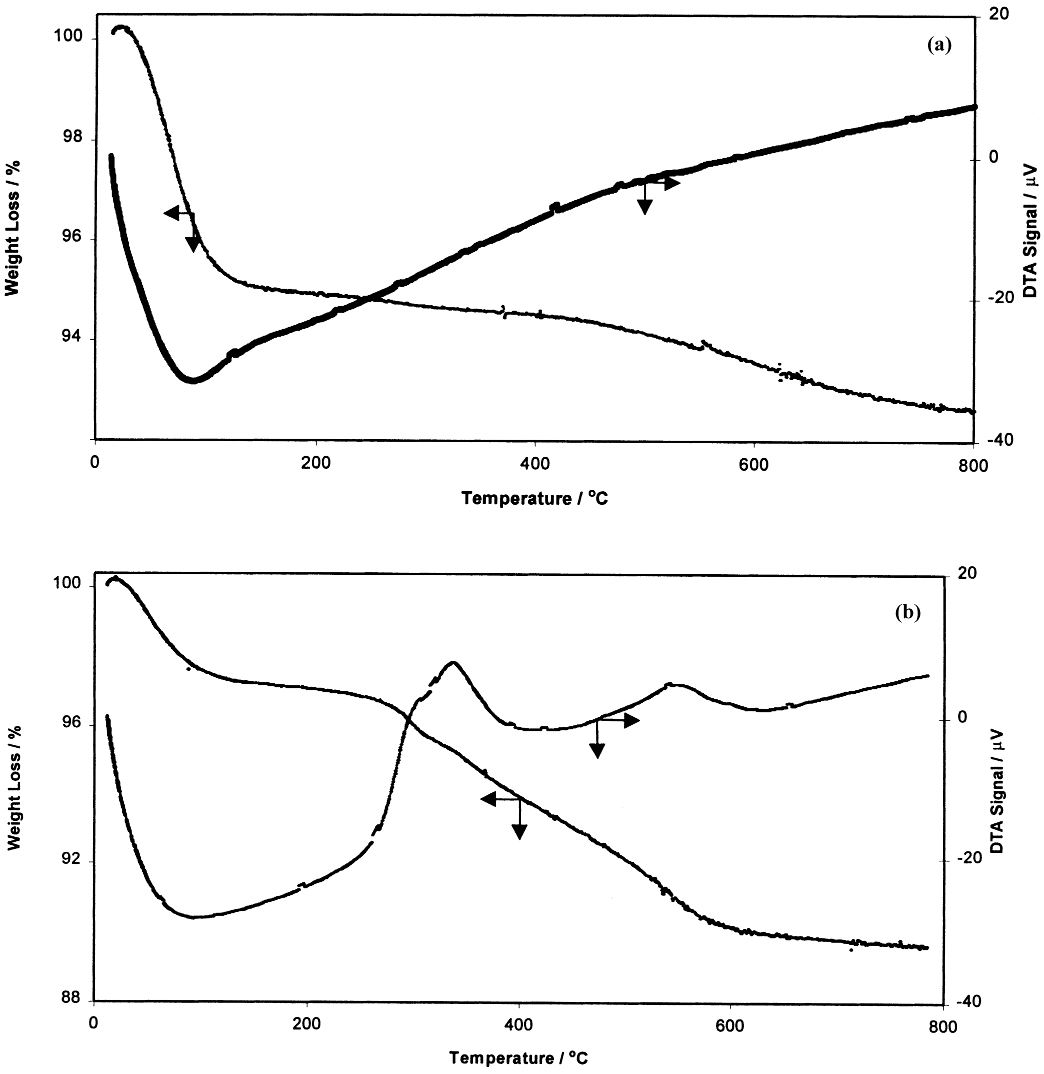


Fig. 1. TGA/DTA signal as a function of temperature for (a) UHPV silica and (b) modified-UHPV silica.

ment. There was 8% weight loss from TG analysis, associated with combustion of the silica anchored surfactant, which is higher than the theoretical coverage of all the surface SiOH group with APTES (<3% in the actual TG measurement) implying that the subsequent attachment had been achieved.

The BET surface area and the pore size analysis (Fig. 2a and b) were also consistent with the chemical modification of silica surface with organic groups. The surface area decreased from 304 to 223 $m^2 g^{-1}$ with a significant decrease in the pore volume at 20 nm and the appearance of a shoulder at smaller pore size of 16 nm.

3.2. Catalysis

From our preliminary investigation as seen in Table 1, we demonstrate that the SAP methodology on silica surface can be applied to the molybdate (ammonium molybdate is a water-soluble species) catalysed epoxidation of cyclohexene with TBHP in bulk dichloromethane. In the presence of small amounts of

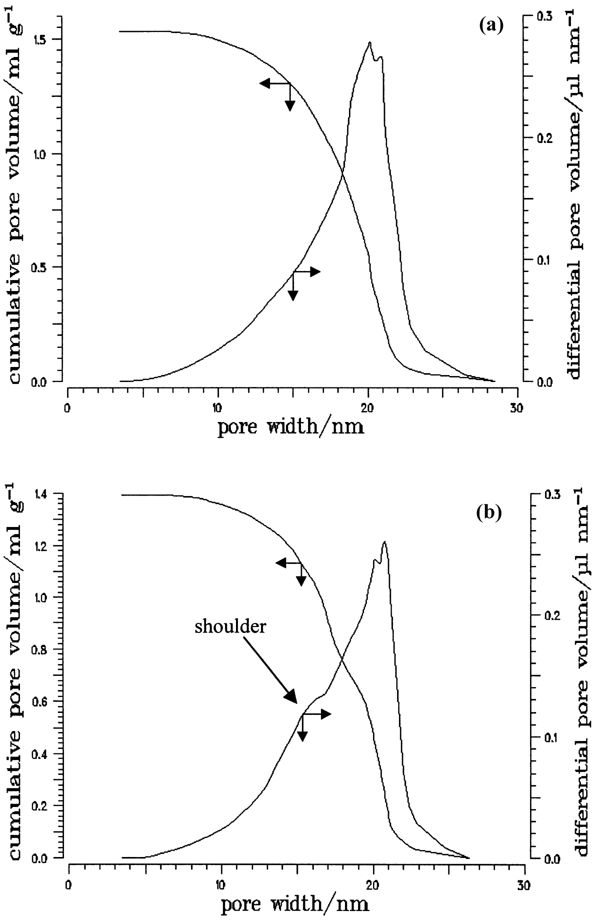


Fig. 2. Pore size distribution for (a) UHPV silica and (b) modified-UHPV silica.

water (11–26%), as thin films on the silica surface, TBHP conversions of around 45–50% with selectivity of >90% for cyclohexene oxide were achieved. In contrast, the dry supported molybdate catalyst in dichloromethane is inactive, indicating that a minimum amount of water is necessary to observe decent catalytic activity. This is a phenomenon attributed to a certain mobility of the molybdate species on the surface of the silica. With a greater amount of water (over 40% w/w), the activity dramatically decreased approaching the value obtained using two biphasic layers; this phenomenon was commonly observed in the SAP systems and was attributed to plugging the pores with water, leading to much longer diffusion paths [4,5].

Table 1 also shows the comparison of the catalytic activity of SAP on unmodified silica to the silica tethered with surfactant molecules. It is interesting to note that a significantly higher activity (92.2 vs 44.3%) is obtained using surfactant modified-silica than unmodified silica with comparable water contents. Mesoporous silica MCM41 with higher BET surface area (1170 $m^2 g^{-1}$) and well-defined channels (of about 4 nm) was also investigated [9]. It was found that MCM41 tethered with surfactant molecules also showed higher catalytic activity (79.7 vs 21.0%) than unmodified MCM41 silica. This indicated that the supported surfactant assemblies within the channels neither fill up the pores nor create tremendous mass transfer problems as compared with the unmodified MCM41 although its activity is poorer than the silica-surfactant sample. In general, these results support our original hypothesis which state that the

Table 1
Comparison of catalytic activity in terms of TBHP consumption using different catalyst systems

Catalyst system	Conversion of TBHP after 24 h (%)
Two biphasic layers (15 cm^3 water and 15 cm^3 dichloromethane)	2.5
SAP on silica	
Dried by evaporation	1.5
14.1% H_2O	*44.3*
20.5% H_2O	52.9
26.1% H_2O	47.8
45.5% H_2O	2.8
SAP on silica-surfactant (11.1% H_2O)	*92.2*
SAP on MCM41 (H_2O not determined)	21.0
SAP on MCM41-surfactant (H_2O not determined)	79.7

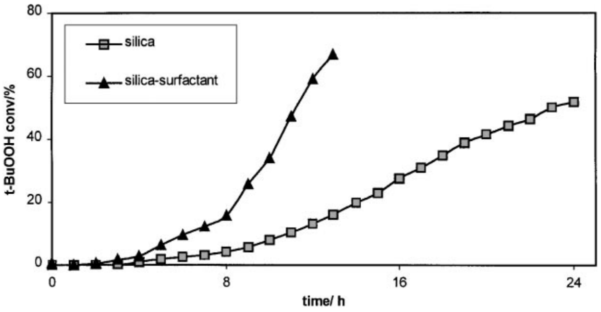


Fig. 3. Rates of TBHP consumption of SAP on silica and SAP on silica-surfactant at different reaction times.

Table 2
The effect of water contents on catalytic activities and selectivities of the cyclohexene oxidation using the SAP–silica-surfactant system

Reaction after 24 h	Water content SAP–silica-surfactant (%)				
	11.1	19.6	26.0	42.5	>60
TBHP conversion (%)	87.6	95.4	85.6	29.2	<1
Selectivity (%)					
Cyclohexene oxide	93.2	92.8	95.3	67.0	–
2-Cyclohexene-1-ol	5.3	5.6	3.2	20.6	–
2-Cyclohexene-1-one	1.5	1.6	1.5	12.4	–

attachment of surfactant molecules to the surface of a SAP catalyst would increase the mass transfer across the aqueous–organic interface.

Fig. 3 illustrates the difference in rates for oxidation of cyclohexene by the two systems (SAP on silica and SAP on silica-surfactant) as a measure of the consumptions of TBHP. There was roughly a 2 h induction period for both of the systems before any oxidised products was observed. The precise reason for an induction period is not yet known, however, we believe the phenomenon is a complex one and could be due to the fact that sufficient products have to be made in excess to the solubility limits in the supported thin water film. Another possible reason is the optimised accumulation of water (by-product from unselected cyclohexene oxidation) for the optimum catalysis to occur. Therefore, it is of no surprise to observe an induction period for the working catalysts. Kinetic analysis of the rates of consumption of TBHP between 8 and 13 h indicated that the SAP on silica gave 2.4% TBHP conversion per hour with a TOF of 0.66 h^{-1} per molybdate species, while the silica-surfactant sample gave about 10.4% TBHP conversion per hour with a TOF of 2.86 h^{-1}. While the particular catalytic reaction has not yet been optimised the results clearly show the trend of tethering surfactant molecules on silica can promote the rate of oxidation by at least 4.4 times. These TOF compare favourably with typical published data for Ti-MCM41 catalysed cyclohexene epoxidation using TBHP, which gave TOFs ranging from 1.5 to 4 h^{-1} per Ti site [10]. Although we have not yet obtained direct evidence to show that the supported organic molecules actually forming ‘micellar structures’, the results strongly imply that the supported organic molecules aggregate in a manner akin to micelle formation in the liquid phase on a solid surface. These include the utilisation for an intrinsically ‘water-soluble’ ammonium molybdate as a catalyst in pure organic solvent and the activity enhancement associated with the use of surface anchored surfactant molecules. Physical characterisation of the novel supported micellar structure such as small angle neutron scattering and cryogenic solid state NMR experiments are in progress.

Akin to the SAP on unmodified silica, Table 2 clearly show that catalytic activities and selectivities of the supported aqueous phase containing soluble molybdate on the silica-surfactant assemblies depends on the water contents of the system. Small amounts of water (11–26%) are necessary to create water film/droplets together with the surface surfactant assemblies in the microenvironment such that high activities were obtained with high selectivity to the epoxide (cyclohexene oxide >92%). Again, the high activity indicates that tethered surfactant molecules enhances mass transfer between the hydrophobic and hydrophilic species through a surface supported micellar microenvironment which also serves to separate the catalyst and the reaction components. The high selectivity to epoxide suggests a very selective oxygen transfer mechanism from TBHP to double bond by the molybdate species which is carried out in polar medium instead of the radical reactions (H-abstraction from cyclohexene) favourably occurred in a relatively non-polar medium. Above these quantities of water (>40%) significant attenuation in catalytic activities were observed. It is also noted that the product selectivity was dramatically altered when a high water

Table 3
The repeatability of the SAP–silica-surfactant system for cyclohexene oxidation

Run	Mo content (ppm)[a]	TBHP conversion (%)	Selectivity (%)		
			Cyclohexene oxide	2-Cyclohexene-1-ol	Cyclohexene-1-one
1	37.5	92.2	92.4	5.7	1.9
2	37.0	90.1	93.9	4.9	1.2
3	–	87.9	95.9	1.9	2.2
4	35.4	88.2	96.0	1.7	2.3

[a] The Mo content was analysed by atomic absorption through an initial dissolution of 0.10 g catalyst into aqua regia (20 cm^3) for 24 h and diluted to 100 cm^3 with DI water where 5 cm^3 of which was further diluted into 50 cm^3 prior to analysis.

content (42.5%) silica-surfactant sample was used. The reason is not yet known, however, it could be due to the relative solubility of products in water film and in bulk dichloromethane (products in organic phase were only analysed) at the particular high water content and at low conversions conditions.

Preliminary tests of recycling of SAP–silica-surfactant sample indicate no dramatic deactivation although there are very slight, if it is significant, drop in activity with the number of runs (Table 3). This could be due to either a very slight progressive leaching of molybdate species in the solution (which is certainly low if one considers that the marginal changes in the Mo contents and the catalytic activity) and/or a progressive loss of water to the bulk organic solvent. Studies on the long term deactivation, catalyst and water leaching and preparative methods to reduce deactivation are currently underway.

4. Conclusions

We have shown for the first time, that a simple metal salt (ammonium molybdate), can be used as a selective oxidation catalyst in bulk dichloromethane, when carried on a solid surface by a water film/droplets. The cyclohexene oxidation using the SAP–silica-surfactant system proceeds with a rate significantly greater than the SAP catalyst on unmodified silica, which in turn has a greater rate of conversion than a simple stirred biphasic system. This clearly suggests anchored surfactant molecules play an active role in enhancing the catalytic activity. Multiphasic catalysis with addition of surfactants has been previously studied [11]. Owing to their dual hydrophobic and hydrophilic character substantial rate enhancement in reactions of hydrophobic and hydrophilic species has been reported [12]. However, few applications of using unbound surfactants have been developed because of the separation problems. We now demonstrate a novel way of improving the SAP by using supported surfactant assemblies. Our results clearly implies that catalysis occurred within the small surfactant assemblies as *nano-reactors*, hence the following advantages are encountered:

1. optimising interfacial area between two immisible solvents;
2. enhanced solubility of hydrophobic substrates in aqueous phase by the supported surfactants;
3. can turn the intrinsic liquid–liquid batch processes to a continuous process.

To conclude, the concept of using chemically supported micelles as nano-reactors for biphasic oxidation catalysis is new and has not been reported in the open literature. The preliminary results presented in this paper suggest that this could be a very fruitful area for future research into clean organic oxidation catalysis. The supported micellar microenvironment would alleviate, if not completely solve, the current problems associated with the SAP catalyst approach: transfer problems of hydrophobic–hydrophilic species; difficulties in controlling water content; leaching of water and catalysts, etc. Detailed study of this new system is currently under investigation.

References

[1] B. Driessen-Hölscher, Adv. Catal. 42 (1998) 473.
[2] K.T. Wan, M.E. Davis, J. Catal. 148 (1994) 1.
[3] K.T. Wan, M.E. Davis, Nature 370 (1994) 449.
[4] M.S. Anson, M.P. Leese, L. Tonks, J.M.J. Williams, J. Chem. Soc., Dalton Trans. (1998), 3529.

[5] S.D. Santos, Y. Tong, F. Quignard, A. Choplin, D. Sinou, J.P. Dutasta, Organometallics 17 (1998) 78.
[6] R.A. Sheldon, J. Mol. Catal. A 107 (1996) 75.
[7] P. Sutra, D. Brunel, J. Chem. Soc., Chem. Commun. (1996) 2485.
[8] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.
[9] R. Burch, N.A. Cruise, D. Gleeson, S.C. Tsang, Chem. Commun. (1996) 951.
[10] L.J.Chen, G.K. Chuah, S. Jaenicke, Catal. Lett. (1998) 107.
[11] G. Oehme, I. Grassert, S. Ziegler, R. Meisel, H. Fuhrmann, Catal. Today 42 (1998) 459.
[12] J.H. Fendler, Acc. Chem. Res. 9 (1976) 173.