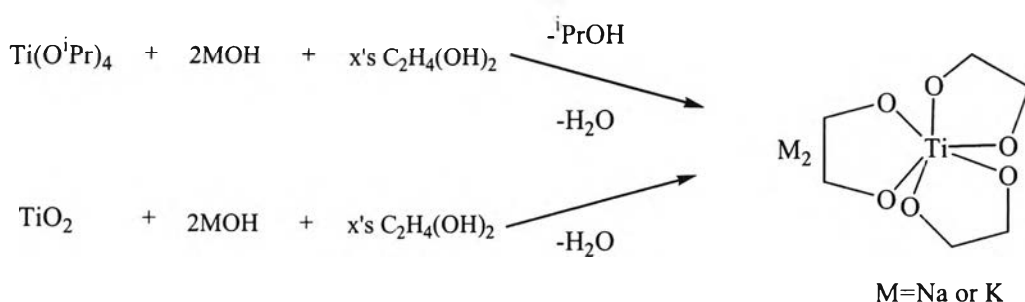# CHAPTER II

LITERATURE SURVEY

2.1 Synthesis of Metal Alkoxides

The metal alkoxide precursors for catalyst synthesis are of interest to study because of their remarkable ability as precursor for electroceramic materials. Apparently, the synthesis of new metal alkoxides possessing unique structures and properties is of great significance for the investigation of sol-gel process as well as the evolution of metal alkoxide chemistry. However, there are some disadvantages of metal alkoxides that make it difficult to study their structures and properties thoroughly, such as, the extreme moisture sensitivity and the tendency to form mixtures of structurally complex species upon hydrolysis. From these reasons, many literatures tried to improve the properties of metal alkoxide, such as, the synthesis of anionic titanium tris(glycolate) complex from reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxide, as shown in scheme 2.1. (Grainsford $et\ al.$, 1995)

$$Ti(O^iPr)_4 \quad + \quad 2MOH \quad + \quad x's\ C_2H_4(OH)_2 \xrightarrow[-H_2O]{-^iPrOH}$$

$$TiO_2 \quad + \quad 2MOH \quad + \quad x's\ C_2H_4(OH)_2 \xrightarrow[-H_2O]{}$$

M=Na or K

Scheme 2.1   The preparation of synthesized anionic titanium tris(glycolate) complex.

The hydrothermal reaction of titanium tetraethoxide, n-butylamine and glycol to obtain titanium glycolate complex was successful after the reaction at 160°-180°C for 5 days. The product exhibited outstanding high stability not only in alcohol but also in water (scheme 2.2). (Wang $et\ al.$, 1999)

$$Ti(OC_2H_5)_4 \quad + \quad x's\ HOCH_2CH_2OH \quad + \quad CH_3(CH_2)_3NH_2 \longrightarrow$$
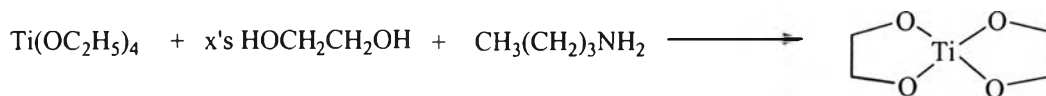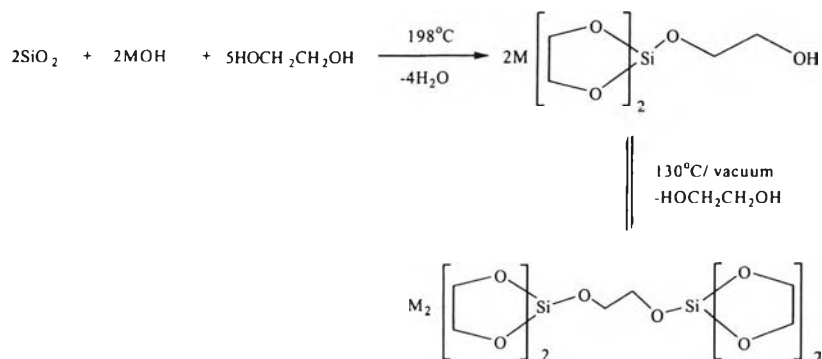
Scheme 2.2 The preparation of titanium glycolate complex by reacting titanium tetraethoxide with glycol.

The silatrane complex was synthesized by direct reaction of SiO_2 and triisopropanolamines. The precursor exhibited the outstanding high stability not only in alcohol but also in water and was synthesized from inexpensive starting materials as scheme 2.3. (Wongkasemjit *et al.*, 2001)

$$SiO_2 + N(CH_2CHCH_3OH)_3 + H_2NCH_2(CH_2NHCH_2)_2CH_2NH_2 + HOCH_2CH_2OH$$
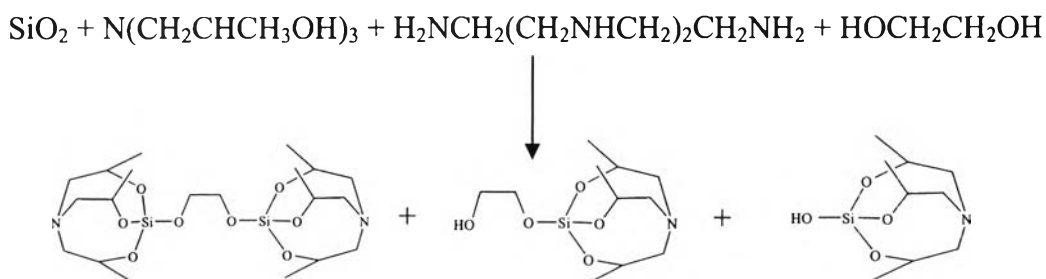
Scheme 2.3 The preparation of silatrane complexes by Wongasemjit's method.

The oxide one pot synthesis (OOPS) process was used to investigate a straightforward and low-cost route to produce alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol, as shown in scheme 2.4. (Laine *et al.*, 1991)

$$2SiO_2 \quad + \quad 2MOH \quad + \quad 5HOCH_2CH_2OH \xrightarrow[-4H_2O]{198°C}$$

130°C/ vacuum
$-HOCH_2CH_2OH$

Scheme 2.4 The preparation of siloxane complex by the reaction of SiO_2 and glycol.

The synthesis of titanium tetraethoxide (Ti(OEt)$_4$) and titanium tetrapropoxide (Ti(OPr^n)$_4$) was studied by the reaction of hydrous titanium dioxide (TiO$_2$.nH$_2$O, n=0.15-1.23) and dialkyl carbonates using various alkali-metal hydroxides catalyst (LiOH, NaOH, KOH and CsOH) as scheme 2.5. The reaction was carried out in autoclave at a heating rate of 90 Kh^{-1}. They reported that use of sodium hydroxide gave the highest yield compared to the others. (Suzuki *et al.*, 1997)

$$TiO_2.nH_2O \ + \ (2+n)R'OC(=O)OR' \longrightarrow Ti(OR')_4 + (2+n)CO_2 + 2nR'OH$$

(when R' = Et, Pr^n)
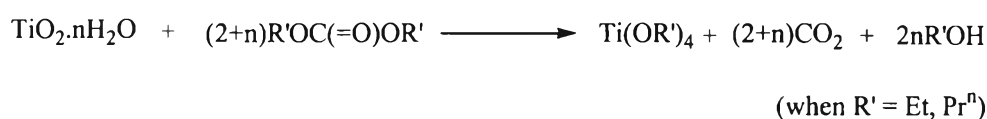
Scheme 2.5   The preparation of titanium tetraethoxide (Ti(OEt)$_4$) and titanium tetrapropoxide (Ti(OPr)$_4$).
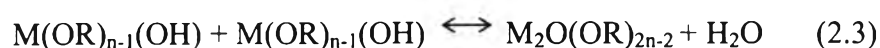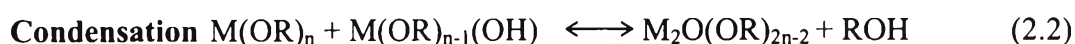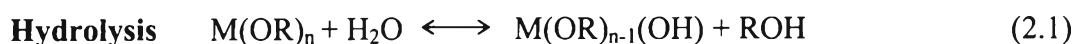
2.2 Sol-gel Process of Metal alkoxides

Sol-gel technique has been extensively used to prepare amorphous and crystalline materials. In general, the sol-gel process is the synthesis of an inorganic network at low temperatures by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Generally, the precursor is dissolved in a suitable organic solvent in order to form a solution. The solvent must be carefully selected so that a solution with high concentration of the required component is obtained. Sol- gel processing involves the following steps:

1.   precursor formation
2.   hydrolysis to form solution (sol)
3.   polycondensation
4.   film and gel formation
5.   organic pyrolysis by heat treatment

6.   densification and crystallization by annealing process

There are two important reactions in polymeric gel formation. These reactions are partial hydrolysis, followed by condensation polymerization. Polymerization steps via hydrolysis and condensation reaction are illustrated (Budd, 1986), as follows (Yi and Sayer, 1991):

Hydrolysis $M(OR)_n + H_2O \longleftrightarrow M(OR)_{n-1}(OH) + ROH$ (2.1)

Condensation $M(OR)_n + M(OR)_{n-1}(OH) \longleftrightarrow M_2O(OR)_{2n-2} + ROH$ (2.2)

$M(OR)_{n-1}(OH) + M(OR)_{n-1}(OH) \longleftrightarrow M_2O(OR)_{2n-2} + H_2O$ (2.3)

The M-O-M network product is formed by polycondensation reactions, as shown in Reactions 2.2 and 2.3 in which alcohol and water are produced as the by-products. These reactions lead to a degree of gelation regarding to the appropriate amount of water. Other critical parameters usually considered are viscosity of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are employed to improve spin ability and coating ability. In addition, solution concentration, viscosity, surface tension of the solution and the deposition technique determine the film thickness and uniformity.

In general, the sol-gel process gives high surface area, pore structure, homogeneous property of the products and moreover it is a low-temperature method for converting metal alkoxide to metal oxide. There are many works investigated the sol-gel process using various type of precursors for certain properties.

Previously, the mesoporous nanocrystalline TiO_2 was prepared by a sol-gel technique using butanediol mixed with tetrapropylorthotitanate and aged in ambient temperature for 1-8 weeks. A highest surface area of 97 m^2/g and diameter 10 nm were obtained after calcination at 400°C for 2h. The aging time and calcination temperature influence the phase transformation of nanophase titanium dioxide which the phase transition of anatase to rutile began at 630°C and was complete at 730°C. (Zhang *et al.*, 2002)

The forced hydrolysis of boiling reflux method of $Ti(SO_4)_2$ solution in the presence of a small amount of H_2SO_4 was used to prepare nanodispersed spherical

TiO_2. The particle size distribution was over 100 nm. The inhibition of H_2SO_4 to phase transformation causes the nucleation rate to slow down. When the concentration of H_2SO_4 continues to rise, the particle size increases and the production of TiO_2 powder is reduced dramatically. (Wei et al., 1999)

The MOCVD (molecular chemical vapor deposition) technology was used to synthesize nanosized anatase titania. The titanium tetrabutoxide was pyrolyzed in an oxygen-containing atmosphere and the average grain size ranging from 7.4 to 15.2 nm was observed. The preparation temperatures not only accelerate the nucleation rate but also the particle growth rate. The smallest average grain size 7.4 nm and the highest surface area 180 m^2/g were obtained at 700°C. The anatase-rutile transformation temperatures were about 700°-1000°C. (Sun et al., 2001)

The hydrolysis of titanium tetraisopropoxide (TTIP) in the aqueous cores of water/NP-5/cyclohexane microemulsion was used to synthesize ultrafine titania particles. With increasing calcination temperature from 300° to 700°C, the specific surface area of the TiO_2 particles decreased from 325.6 to 5.9 m^2/g, whereas the average pore radius increased from 1.4 to 25.1 nm. The particles calcined up to 300°C indicated that they are amorphous and upon increasing the temperature to 650°C, the rutile peaks appeared. (Kim et al., 2001)

The sol-hydrothermal method using titanium n-butoxide (TNB) precursor in various acidic media (HCl, HNO_3, H_2SO_4 and CH_3COOH) was used to synthesize nanocrystalline titanium dioxide. The nanocrystals of pure rutile with size < 10 nm were obtained at higher HCl concentrations under mild conditions. The propensity of acidic medium for rutile formation is shown as follows: HCl > HNO_3 > H_2SO_4 > HAc. (Wu et al., 2002)

The mesoporous spherical titania particles were prepared via hydrolysis of pure titanium tetra-isopropoxide in n-heptane solution. Calcination of hydrolyzed product produced pure anatase at 400°-600°C and rutile at 800°C. The highest specific surface area of 132 m^2/g and pore size of 10 nm were obtained at 400°C which are higher than that of material calcined at 600°C (58.5 m^2/g) and much higher than that of the material calcined at 800°C (5.0 m^2/g). (Khalil et al., 2001)

Nanosized titanium(IV) oxide in the anatase form was synthesized by hydrolysis of titanium n-butoxide in toluene with water at high temperature (150-300

°C) The crystalline size of the anatase was gradually increased with reaction temperature and reaction time. The surface area of 71 m^2/g was received after calcination at 700 °C and the transformation temperature from anatase to rutile was at around 1000°C.(Kominami *et al.*, 1999)

2.3 The Rheological Study of Metal Alkoxides

Chambon and Winter, proposed a constitutive equation for linear viscoelasticity of incipient gels, which they called the gel equation.

$$\delta(t) = S \int_{-\infty}^{t} (t - t')^{-n} \gamma(t') dt' \qquad (2.4)$$

where δ is the shear stress, γ is the rate of deformation tensor, n is the relaxation exponent and S is the gel strength parameter (with dimensions $Pa.s^n$), which depends on the cross-linking density and the molecular chain flexibility. A more general version of this model has been developed, where the model proposed by Winter and Chambon constitutes a special case.

The storage modulus G' and the loss modulus G" at the gel point both will follow similar power laws in frequency,

$$G' = G''/\tan \delta = S \omega^n \Gamma(1-n) \cos \delta \qquad (2.5)$$

where $\Gamma(1-n)$ is the gamma function. The phase angle between stress and strain (δ) is independent of frequency but proportional to the relaxation exponent,

$$\delta = n \pi/2 \qquad (2.6)$$

This result suggests that the power law behavior of the dynamic moduli can be expressed as

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (2.7)$$

Theoretical models have been elaborated to rationalize values of the relaxation exponent in the physical accessible range $0 < n < 1$. In the theoretical

advances, based on the fractal concept, the dynamic exponent n is associated with information about the molecular structure and connectivity of the incipient gel.

The structure may be described by a fractal dimension d_f, which is defined by $R^d_f \sim M$, where R is the radius of gyration and M is the mass of a molecular cluster. On the basis of the percolation approach, the Rouse model, which assumes no hydrodynamic interaction between polymeric clusters, predicts $n = d/(d_f + 2)$ and with $d = 3$ (the space dimension) and $d_f = 2.5$ (percolation statistics) n assumes a value of 0.67. In the electrical analogy, a suggested isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors yields a value of $n = 0.72$.

If we consider a situation where the strand length between cross-linking points of the incipient gel varies, one may anticipate that increasing strand length should enhance the excluded volume effect. In order to take this into account, Muthukumar suggested that if the excluded volume interaction is fully screened, the scaling exponent can be expressed as

$$n = d(d + 2 - 2d_f)/2(d + 2 - d_f) \qquad (2.8)$$

Quite recently, the relation between the viscoelastic and structural properties of systems of cross-linking polymers near the gel point was considered in the framework of a mechanical ladder model, which predicts a scaling law for the complex shear modulus with an exponent $0 \leq n \leq 0.5$. It was shown that the parameter n is related to the spectral dimension $d_s \geq 1$ of the fractal through the relationship.

$$n = 1 - d_s/2 \qquad (2.9)$$

2.4 The Synthesis of TS-1 Zeolite

Since 1987 that Taramasso et $al.$ discovered the TS-1 zeolite, there are many researchers tried to synthesize TS-1 with improving the Ti containing in the zeolite framework by different methods and materials because of the high efficiency and

molecular selectivity in oxidation reactions employing H_2O_2 such as the conversion of ammonia to hydroxylamine, secondary alcohols to ketones, secondary amines to dialklyhydroxylamines, or reactions, such as the hydroxylation, the olefin epoxidation, or the cyclohexanone ammoximation. (Marra *et al.*, 2000)

The effect of organic amine to the formation of TS-1 zeolite was studied with various types of amine which are n-butylamine, TEAOH, TBAOH, 1,6-hexanediamine, ethylenediamine, diethylamine and triethanolamine. To decrease the cost, TPABr was used as a template instead of TPAOH. The $Ti(OC_4H_9)_4$ was used as the titanium source with the ratio of Si/Ti = 33. They found that the organic amine cannot act as a template in the presence of TPA^+. It can only regulate the basicity of the gel. The order of the template effect of different templates is as follows: TPA^+>TBA^+>TEA^+>>organic amine. (Wang *et al.*, 1999)

The synthesis of TS-1 in fluoride medium was prepared by two different methods, mixed alkoxide and wetness-impregnation method. The preparation of a sol or a gel containing Si-O-Ti bonds prior to fluoride addition is the key step of the synthesis. The mixed alkoxide method used TPAOH+HF and the wetness-impregnation used TPABr+NH_4F and the mixture after addition of fluoride was transferred to Teflon-lined autoclave at 170°C for 5 days. The DR-UV result of mixed alkoxide method showed that the samples at Si/Ti ratio 42 showed only the band at 220 nm, indicating that all the titanium is in the zeolite framework. For the wetness-impregnation method, the sample with Si/Ti ratio 90 exhibited only a strong band at 220 nm. (Grieneisen *et al.*, 2000)

Titanium silicate-1 (TS-1) was synthesized in the presence of small amount of TPAOH using tween 20, as nonionic surfactant. The mixture was crystallized at 140°C for 18h under autogeneous pressure at the Si/Ti ratio 33. The result from DR-UV showed a charge transfer band at 220 nm, which is a characteristic of isolated framework of Ti^{4+}. The sample prepared without the use of surfactant, on the other hand showed the band at 330 nm, which suggest the presence of extra framework of TiO^2. (Khomane *et al.*, 2002)

The crystallization kinetics of TS-1 zeolite using quaternary ammonium halides (TEACl+TBACl) as template was studied. TEOS and TBOT were used as a

source of silica and titanium and the crystallization was carried out statically at 160°C for 6-10 days. From the kinetics study of crystallization, as increasing the temperature of crystallization the induction period decreased and the crystallization rate increased. With the increasing of Si/Ti ratio in reaction mixture, the crystallization rate increased and the mean crystal size decreased gradually. The crystallization rate was also depend on the (TEA+TBA)/Si ratio, which increasing he (TEA+TBA)/Si ratio lead to the increasing of crystallization indicating that more template molecules are advantageous to the crystallization of TS-1. The dilution of the sol mixture with water decreased the rate of crystallization and increased the average crystal size. When increasing the NH3/Si ratio, both the rate of crystallization and the crystallinity of the final product were increased. (Xia *et al.*, 1997)

The microwave-assisted synthesis of molecular sieves is a relatively new area of research. It offers any distinct advantages over conventional synthesis. They include rapid heating, resulting in homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels, and eventually a shorter crystallization time compared to those of conventional autoclave heating. Furthermore, it is energy-efficient and economical. (Newalkar *et al.*, 2001) It has been postulated that the major mechanism of microwave heating is due to dipole orientation and ionic conduction. However, if one is pressed to explain the mechanism of microwave heating for a given compound, one cannot clearly explain it with the kind of motion of polar molecules and/or ions. (Ohgushi *et al.*, 2001)

Aluminophosphate molecular sieves (AlPO$_4$'s) were prepared by microwave heating without using organic template reagent. The microwave enhanced the crystallization of aluminophosphate gels, and AlPO$_4$ were successfully obtained as single phase in a relatively short reaction time. (Kunii *et al.*, 2002)

The agglomerated uniformly sized zeolite Y was prepared in a microwave oven in 10 min, whereas 10-15 h was required for the conventional heating techniques depending on the lattice Si/Al ratio. Relatively high Sj/Al ratio, up to 5, could be obtained from hydrogels containing low aluminum contents without

crystallization of undesired phases. ZSM-5 could also be synthesized in 30 min at 140°C by this technique. (Arafat *et al.*, 1993)

The effect of the variation in alkoxide precursor ratio and templating agent concentration on the production of titanium silicate (TS-1) was investigated through analysis techniques. Across the range of compositions studied, x-ray diffraction indicated that all the samples have the MFI crystalline structure and together with Raman, demonstrated incorporation of titanium in the zeolite framework. Energy dispersive X-ray analysis showed that samples produced using an ultra-low alkali metal content templating agent generally resulted in a higher degree of titanium incorporation in the zeolite framework. (Li *et al.*, 2002) The IR spectra showed the characteristic of TS-1 at 960 cm^{-1} and DR-UV at 210 nm which is attributed to tetra-coordinated titanium. (Wang *et al.*, 1999)

2.5 The photoctalytic membrane reactor

The nanostructured mixed matrix membranes were synthesized using the method based on interfacial crosslinking or copolymerization. To prepare the capsules, an AB-type block copolymer surfactant ($MMA_{10}MAA_8$) was employed that consist of ten methylmethacrylate and eight methacrylic acid units. At high pH, $MMA_{10}MAA_8$ is soluble in water and stabilizes w/o emulsions. Capsules were prepared by crosslinking the MAA group of neighbouring surfactants with hexanediamine. The membrane was formed using polymerization of capsules containing monomer combined with the interfacial crosslinking encapsulation method which consisted of a mixture of 70%MMA and 30%MAA. The polymerization reaction was initiated by photo-initiator DMPA in combination with UV-light. The capsules containing films were prepared by dispersing the dry $MMA_{10}MAA_8$ capsules and were dispersed in the MMA/MAA mixture. (Figoli *et al.*, 2002)

The accessible pore system of polymeric ultrafiltration membranes was modified by titanium dioxide and treated further with palladium acetate to yield catalytically active, porous nanofiltration membrane. To overcome the drawback of low thermal stability of common polymeric membranes, the inorganic filler was

added to the membrane casting solution. Polyacrylonitrile (PAN), polyetherimide (PEI) and polyamideimide (PAI) were chosed as polymers. The pore system of membranes was modified by two-step procedure to produce catalytically active membranes for heterogeneous catalysis in gas or liquid phase. In the first step, the pore system was narrowed by creating an inorganic titanium oxide layer on the inner surface of the pores by dipped into a solution of 3.5 wt.% tetraethyl titanate in n-hexane. A second step produced an active layer of palladium on the top of these inorganic modified pores of the membrane. The introduction of the catalyst was performed by treating of the titanium dioxide modified membrane with a solution of 3 wt.% palladium acetate in methyl ethyl ketone (MEK). (Ziegler *et al.*, 2001)

Random copolymers of 2-hydroxyethyl acrylate (HEA) and methyl acrylate (MA) and homopolymer PHEA were prepared by free radical polymerization. The hydroxyl groups of PHEA were reacted with 3-(triethoxysilyl)propyl isocyanate to introduce triethoxysilyl (TREOS) groups. Co-hydrolysis and condensation of the TEOS groups with titanium tetrabutoxide yielded polymer/SiO_2/TiO_2 hybrid materials. At TiO_2 less than or equal to 7.4%, the hybrid membranes produced were transparent. Ti-specific imaging demonstrated that the TiO_2 phase was nano-sized and distributed uniformly inside the polymer matrix. Water vapor permeability across such hybrid membranes could be changed by varying the PHEA content and was very high for PHEA/SiO_2 membranes. The incorporation of MA into the hybrid allowed to reducing membrane swelling by water at no cost to membrane brittleness. (Lu *et al.*, 2003)

Mixed matrix membranes of 6FDA-6FpDA-DABA, a glassy polyimide and modified zeolites (ZSM-2) were fabricated. The ZSM-2 zeolites were functionalized with amine groups by reacting them with aminopropyltrimethoxysilane in toluene. The amine-tethered zeolites interacted through secondary forces with the carboxylic groups along the polymer backbone, as documented by FTIR. Band shifts associated with hydrogen bonding of the carbonyl and amine groups were observed in the spectra. These interactions promoted adhesion between the two components. The solubility coefficient for each gas (CO_2, O_2, N_2, He and CH_4) increased, except for N_2, which was largely unchanged. The changes in permeability for each gas

correlated well with the change in the diffusion coefficient. The permeabilities of He, CO_2 and CH_4 all decreased, while O_2 and N_2 increased. (Pechar *et al.*, 2002)

The photocatalytic membrane reactors for degradation of organic pollutants in water were prepared by using 4-Nitrophenol (4NP) as a probe polluting agent and titanium dioxide in suspension was the catalyst. The commercial membranes were; NTR7410 and NTR7450 (Nitto enko), N30F and NF-PES-010 (Hoechst), MPCB0000R98 (SEPAREM). The measured permeate flux was in the range of 5-30 l/h m^2 at 4 bar and all membranes showed both a rejection and capacity to adsorb the pollutant with a transitory phase varing from 80 to 400 min at 4 bar. Three factors, viz. rejection, photocatalytic degradation and adsorption, were able to maintain the 4NP concentration in the permeate at very low values. (Molinari *et al.*, 2001)

The purification of bilge water by a combination of ultrafiltration and photocatalytic process was studied. The separation of oil from bilge water was performed on a laboratory-scale ultrafiltration pilot plant with tubular membranes made from poly(vinyl chloride) (PVC), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF). The examined membranes with MWCO 70 kD for PVC and Pan and 100 kD fo PVDF produced a permeate with an oil content less than 15 ppm. The photocatalytic process was carried out using titanium dioxide based catalyst. The complete decomposition of oil was achieved after 2h for UV illumination using a K-TiO_2 photocatalyst with content amount to 0.8 g/dm^3 and after 3h of UV illumination using 0.8g/dm^3 of KOH/TiO_2 photocatalyst. (Karakulski *et al.*, 1998)

The preparation of polycrystalline TiO_2 samples impregnated with a modified Cu(II)-phthalocyanine (TiO_2-CuPc) is reported along with an investigation on the photocatalytic behavior of this system compared with bare TiO_2 (both in the anatanse and rutile form) and with TiO_2 samples impregnated with not functionalized commercial phthalocyanine (TiO_2-CuPc) or with metal free phthalocyanine (TiO_2-Pc). The photocatalytic degradation of 4-nitrophenol was studied as a probe reaction. The presence of modified CuPc showed to be beneficial only for TiO_2 (anatase) while the commercial not functionalized CuPc also slightly for both TiO_2 (anatase) and TiO_2 (rutile). The metal free Pc did not show any beneficial influence on the photoactivity. A tentative explanation of the beneficial effect due to the presence of the Cu(II)-phthalocyanines both on the initial reaction rate and on the mineralization

process is provided by taking into account intrinsic electronic and physico-chemical properties. (Mele *et al.*, 2002)