

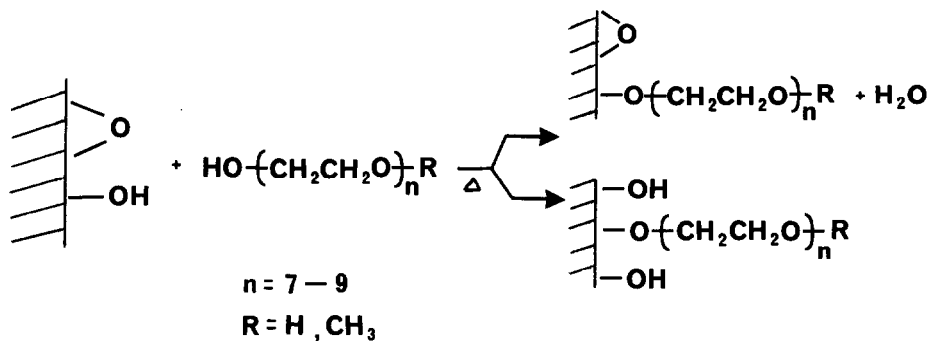
PHASE TRANSFER CATALYSTS
POLYETHYLENE GLYCOLS IMMOBILIZED ONTO METAL OXIDE SURFACES

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Abstract: Catalysts prepared by reacting polyethylene glycol and polyethylene glycol monomethyl ether with both alumina and silica gel were found to be effective phase transfer agents in displacement and oxidation reactions.

The preparation of novel phase transfer catalysts and their application in solving synthetic problems are well documented.¹ Compounds such as quaternary ammonium and phosphonium salts, phosphoramides, crown ethers, and cryptands have been used to catalyze a variety of organic transformations including alkylation, oxidation, and displacement reactions.² Recent efforts have concentrated on the immobilization of these materials onto both organic polymers³ and metal oxides⁴ to simplify, by filtration, the separation and recovery process. We describe herein the preparation of a new catalyst system with phase transfer properties by reaction of a polyethylene glycol and monomethyl ether with alumina and silica gel.⁵

The surface of silica gel contains both silanol-OH groups (mainly responsible for adsorption) and -O- strained siloxane groups.⁶ Surface functionalization of metal oxides such as silica gel is normally accomplished by reaction of various alkyltrialkoxo silanes with the pendant surface hydroxyl groups.⁷ However, alcohols are also capable of reacting directly with the surface either through a dehydration sequence or by direct addition to the strained siloxane moiety.⁸ As polyethylene glycols and monoalkyl ethers have demonstrated phase transfer abilities,^{9,10} and as they possess an alcohol functionality capable of reacting with the surface of a metal oxide, a synthetic scheme (I) was considered wherein direct attachment of the glycol to the support was possible by simple heating. A polyethylene glycol and monomethyl ether were heated in refluxing toluene for 3 hours with both silica gel and alumina¹¹ with continuous removal of the water-toluene azeotrope. After filtering, the white powder was Soxhlet extracted

Scheme I

12 hours with toluene and dried under vacuum. Carbon analysis of the product indicated the degree of functionalization to be between 0.1 and 0.4 mmoles of glycol per gram of support which is typical of metal oxide derivatization (Table I).

TABLE I

<u>Glycol</u> ^a	<u>Support</u> ^b	<u>%C</u>	<u>mmoles Glycol/Gram Support</u> ^c
PEG-400	SiO ₂	6.9	0.33
PEG-400	Al ₂ O ₃	4.1	0.20
PEGMME-350	SiO ₂	7.5	0.36
PEGMME-350	Al ₂ O ₃	3.1	0.17

a) PEG-400 - Polyethylene glycol average molecular weight 400

PEGMME-350 - Polyethylene glycol monomethyl ether average mol. wt. 350.

b) SiO₂ - silica gel, Al₂O₃ - alumina

c) Approximate

The catalysts were subsequently evaluated under phase transfer type reaction conditions. These included the displacement reaction of 1-bromobutane with potassium acetate and the oxidation of benzyl alcohol with sodium hypochlorite solution. Typical reaction conditions follow. A mixture containing 15g (0.15 mol) potassium acetate, 70ml toluene, 20g (0.007 mol) of the PEG-400/SiO₂ catalyst, 7g (0.05 mol) 1-bromobutane and 7g n-decane as an internal standard was heated at reflux for 3 hours. The product was

filtered, washed with methylene chloride and the filtrate analyzed by gas chromatography. The oxidation of benzyl alcohol was carried out by stirring a mixture of 4g (0.04 mol) benzyl alcohol, 75ml methylene chloride, 20g (0.003 mol) of the PEGMME-350/Al₂O₃ catalyst, and 75ml (0.05 mol) of a 4-6% aqueous sodium hypochlorite solution at room temperature for 24 hours. The results are given in Table II.

TABLE II

<u>Catalyst</u>	<u>Reactants</u>	<u>Products</u> ^a	<u>% Yield</u> ^b
SiO ₂ or Al ₂ O ₃	C ₄ H ₉ Br/KOAc	C ₄ H ₉ OAc	0
18-Crown-6	C ₄ H ₉ Br/KOAc	C ₄ H ₉ OAc	54
PEG-400/Al ₂ O ₃	C ₄ H ₉ Br/KOAc	C ₄ H ₉ OAc	32
PEG-400/SiO ₂	C ₄ H ₉ Br/KOAc	C ₄ H ₉ OAc	56
Al ₂ O ₃	PhCH ₂ OH/NaOCl	PhCHO	16 ¹²
TBAHS ^c	PhCH ₂ OH/NaOCl	PhCHO	87
PEGMME-350/Al ₂ O ₃	PhCH ₂ OH/NaOCl	PhCHO	30

a) The products were identical to authentic materials.

b) GC yields.

c) Tetrabutyl ammonium hydrogen sulfate.

These materials have demonstrated their ability to promote phase transfer type reactions. Future work will expand on the synthetic utility of these catalysts.

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