

HETEROGENEOUS PHASE TRANSFER CATALYSTS.

1. SYNTHESIS AND CATALYTIC PROPERTIES OF POLYMERIC CROWN-ETHERS ON INORGANIC SUPPORTS

V. F. Loktev, I. Yu. Morozova,
A. K. Tashmukhamedova, and V. A. Likholobov

UDC 541.128.35:542.91:541.64:547.898

A number of new heterogeneous phase transfer catalysts based on polymeric dibenzo-crown-ethers supported on the carbonaceous material "Sibunite", ultrafine diamonds, or silica gel are synthesized. The activity of several of the catalysts for the reaction of 1-bromooctane with KI is higher than that of previously known analogs. The catalytic effect depends on the support, linker, and solvent.

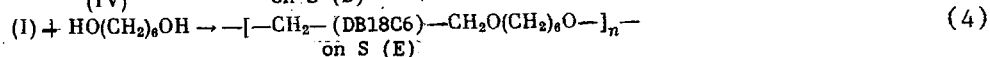
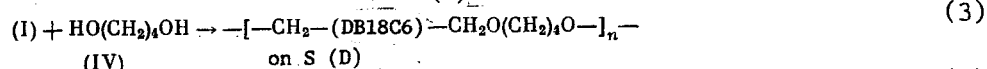
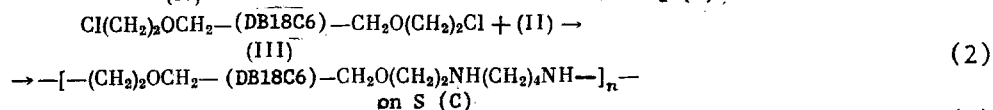
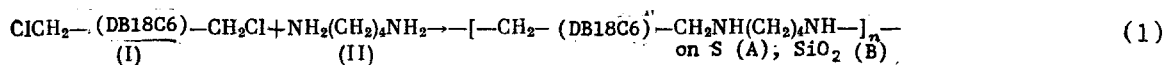
Crown-ethers supported on solids make effective phase transfer catalysts (PTC) that can be regenerated simply compared to homogeneous analogs [1, 2]. One method for heterogenation is to deposit polymeric crown-ethers on organic or inorganic supports that have an active surface [3]. Use of a support enables the consumption of costly monomer to be reduced and the effective catalyst surface and its strength, porosity, etc. to be varied systematically. Moreover, depositing a polymeric crown-ether is usually simpler compared to chemically binding it to the support surface.

The purpose of the present work is to study the dependence of catalytic properties of polymeric crown-ethers on the type of polymer and the nature of the inorganic support.

Carbonaceous supports, in particular "Sibunite" (S) [4] and ultrafine diamonds (UFD) [5] are of definite interest. The value of these supports lies in their high thermal and mechanical strength and their high specific surface area. UFD also are highly resistant to aggressive media. In contrast to silica gel, which is often used as support for PTC, the carbonaceous materials are wetted well by organic solvents. This facilitates catalytic action (cf. [1, 6]). Moreover, the hydrophilic and lipophilic properties of the carbonaceous support surface can be modified chemically [7].

The readily available dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) were used as starting materials. These were previously modified in a number of cases by introducing substituents in the 4',4'' or 4',5'' positions. Polymers with electron-donating substituents on the aromatic rings of DB18C6 or DB24C8 were preferred. Otherwise, the catalytic effect would be diminished [2, 3] (however, cf. [1]).

The polymers were synthesized as follows on the support:*



*Here and henceforth the mixture of isomers 4',4''-di-X- and 4',5''-di-X- dibenzo-18-crown-6 is denoted X-(DB18C6)-X. The corresponding mixture of DB24C8 derivatives is denoted X-(DB24C8)-X.

Institute of Catalysis, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Tashkent State University. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 6, pp. 1257-1262, June, 1990. Original article submitted April 24, 1989.

TABLE 1. Characteristics and Catalytic Activity^a of Phase Transfer Catalysts (PTC)

PTC	S _{sp} , m ² /g	N content, %	Crown content in PTC, mmole/g		1-Iodoctane yield, % ^b	
			from mass increase	from N in- crease	in chloro- benzene	in decane
A	116	0,75	0,26	0,27	22(20)	4(4)
B	333	0,72	0,24	0,26	1	1
C	277	0,68	0,22	0,24	49 ^c	49 ^c
D	353		0,13		22 ^d (28)	3
E	338		0,14		25	11
F	270	0,48	0,20	0,17	2	
G	204	0,60 ^e	0,23	0,21	1	1
H	382		0,06		41	46
I	299		0,06		25(27)	19
J	245		0,13		7(8)	2
K	203		0,18		5(4)	
L	180	1,01 ^e	0,35	0,36		5
DB18C6 ^f					7	
S	540	g			1	1
UFD	390	2,03			1	1
SiO ₂	504	g			1	1

^aFor the reaction of 1-bromooctane (0.5 ml) with KI (1.5 ml saturated aqueous solution), organic solvent: chlorobenzene or decane (1.5 ml); 3 h at 80°C. Amount of catalyst (0.025 mmole) calculated on the basis of crown-ethers.

^bAccording to GLC. Yield in parentheses with catalyst used repetitively. Selectivity in all cases was ~99%.

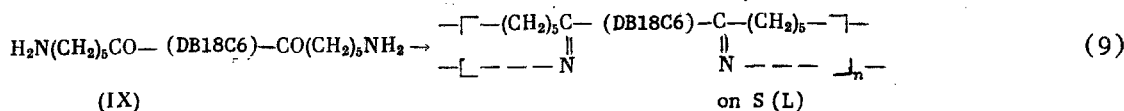
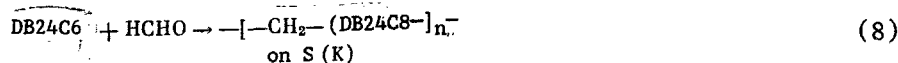
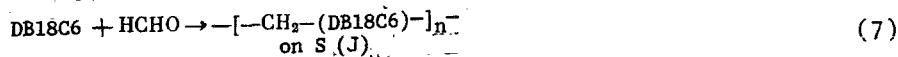
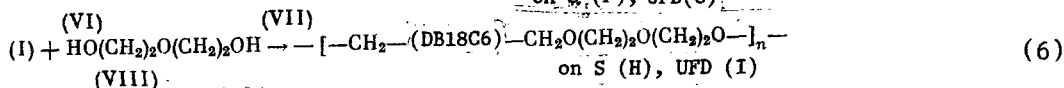
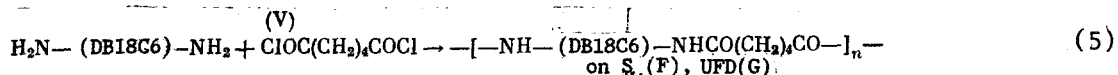
^cYields were 91 (73) in chlorobenzene and 92 (80)% in decane for 0.075 mmole catalyst.

^dAfter 6 h the yield was 56%.

^eIncrease of N content compared to starting UFD.

^fHomogeneous DB18C6 catalyst.

gTrace.



The necessity to cross-link the polymers was considered in choosing the deposition method since the polymers dissolved without it (see Experimental). Cross-linking using schemes (1), (3), (4), and (6) was effected by 4',4'',5'-tris(chloromethyl)DB18C6, which according to PMR data was present as an impurity (5-7%) in the dichloride (I). Cross-linking according to schemes (2) and (5) was achieved by adding 3,4,4'-triaminodiphenyl ether (X) (5 mole %) to diamines (II) and (VI). Formation of tris(methylene)-substituted dibenzo-crown ethers [1] gave cross-linking in schemes (7) and (8). The cross-linked polymer was the principal product of scheme (9).

Formation of polymers containing crowns on the surface of samples B, G, H, and L was demonstrated by signals characteristic of the crown-ethers (1120-1140 and 1240-1260 cm⁻¹, C-O-C; 1420-1430 and 1440-1460 cm⁻¹, -CH₂CH₂-; 1500-1520 cm⁻¹, aromatic ring [3, 8]) in their IR spectra. Signals from bound groups were also present (1660 cm⁻¹, C=N; 1580 and 1710 cm⁻¹, amide group).

IR spectra for polymers on S could not be obtained due to the opacity of the latter in the IR region. However, indirect data are consistent with their formation. Polymerizing treatment in all cases caused the sample mass to increase. The increase was in excellent

TABLE 2. Catalytic Activity Data for Heterogeneous PTC Based on DB18C6 (for reaction of $n\text{-C}_8\text{H}_{17}\text{Br} + \text{KI}$)

Reaction No.	Catalyst ^a	PTC: $n\text{-C}_8\text{H}_{17}\text{Br}:\text{KI}$, mmolar	T, °C	Time, min	Yield, %
1	PS- CH_2OCH_2 -(DB18C6)	1:20:50		40	50 [9]
2	PS- $\text{CH}=\text{CH}$ -(DB18C6)-R ^b	1:50:250	90	60	90
3	$-\text{[-CH}_2\text{-(DB18C6)-C}_6\text{H}_3(\text{OCH}_3)\text{-]}_n\text{-}$	1:9:745		300	32 [10]
4	$-\text{[-CH}_2\text{-(DB18C6)-]}_n\text{-}$	1:7:580		$1.5 \cdot 10^3$	50 [13]
5	(C)	1:115:375	80	300	7
6	(H)	1:38:425		180	49
7	(J)	1:115:375			91
					41
					7

^aPS is polystyrene. For Nos. 1-4, the organic solvent is toluene; for Nos. 5-7, chlorobenzene.

^bR = CHO, CH=CH-PS.

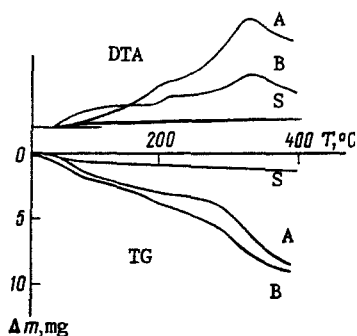


Fig. 1. Thermal analysis curves (decomposition in air) of catalysts A, B, and S.

agreement with the elemental analysis for the catalysts containing nitrogen (Table 1). Polymers with analogous structure can be assumed to exist on the surface of samples A and B based on the similarity in their thermal analysis curves (Fig. 1).

Depositing the polymer decreases the specific surface area S_{sp} of the sample (Table 1). The polymeric particles apparently cover its pores.* Preliminary measurements of the starting S and catalyst A using mercury porosimetry shows that the micropore volume decreases after depositing the polymer whereas the macropore volume is practically unchanged.

Measurements of the polymer particle sizes on the catalyst surfaces using photomicrography were attempted for samples A and B. However, no differences in catalyst surfaces on the corresponding supports could be seen on varying the magnification from $\times 10$ to $\times 8000$. In all probability, either the polymeric particles are located mainly in the support pores or their size is less than 1000 \AA .

The catalytic effect of the samples prepared was studied for the reaction



The corresponding data are given in Table 1.

It is remarkable that the activity of a number of the heterogeneous PTC is much greater than that of the homogeneous analogs (cf. [9, 10]).

The significantly reduced catalytic activity on going from A to B is useful in explaining the dependence of activity on support type. The reason for the reduction might be the increased hydrophilicity of silica gel compared to S [11]. This leads to poorer wetting of catalyst B by the organic solvent and reagent. Also, the support surface during catalyst synthesis may influence the structure of the polymeric particles formed, their size, porosity, etc. Comparison of data for samples F and G and H and I suggests that the catalytic activity for polymers with similar structure falls on changing from S to UFD.

*Pores in UFD are formed at junctions of crystals [5].

TABLE 3. Synthesis Conditions for Phase Transfer Catalysts

Catalyst	Crown-ether, g	Reagent, g	Solvent, ml	Support, g	Reflux time, h
A	(I), 2,8	(II), 0,54	CHCl ₃ , 50	S, 25	10
B				SiO ₂ , 25	
C	(III), 2,8	(II), 0,48	CHCl ₃ , 50	S, 25	10
D	(I), 0,5	(IV), 0,10	Mixture of dioxane: pyridine 50:0.5	S, 0.5	6
E		(V), 0,13		S, 0.5	
F	(VI), 0,4 ^{a, b}	(VII), 0,2	Mixture of hexane: pyridine 25:0.5	S, 4.0	8
G				UFD, 4.0	
H	(I), 0,5	(VIII), 0,12	Mixture of dioxane: pyridine, 50:0.5	S, 0.5	6
I			conc. HCl, 17	UFD, 0.5	
J	DB18C6, 0.45 ^b	HCHO, 0,23		S, 5.0	6(80°)
K	DB24C8, 0.56 ^b				
L	(IX), 0,25	-	CHCl ₃ , 5	UFD, 1.0	1

^aTriamine (X) was also added (5 mole %).

^bThe crown-ether was deposited on the substrate before condensation by evaporating to dryness a mixture of the support and a saturated solution of crown-ether in CHCl₃.

The PTC effectiveness depending on organic solvent is also interesting. For example, the 1-iodooctane yield for samples A and D falls on going from chlorobenzene to decane. A similar dependence was seen earlier for their reactions using PTC [2, 11]. Either no effect or a slight increase in activity was seen for catalysts C and H. This is difficult to explain at present.

The data in Table 1 show that the PTC activity depends substantially on the nature of the fragments binding the crown-ethers. These fragments can control the rigidity of the polymeric chains, the hydrophilicity of the polymeric particles, and their dispersion. Thus, the low effectiveness of catalysts J and K is apparently due to the three-dimensional rigidity of the corresponding polymers caused by the short-cross-links (cf. [1]). A possible reason for the low activity of samples F and G is their weak lipophilicity due to the hydrophilic amides in the binding fragments [12]. Similar effects evidently reduce the catalytic effect of sample L.

Activity data obtained earlier for heterogeneous PTC based on DB18C6 and several samples prepared by us are presented in Table 2. Considering the difference in reaction temperature and PTC:substrate ratio, the activity of samples C and H exceeds that of the analogs described in the literature (without taking into account the dependence of activity on solvent).

It is also significant that the catalytic effect of polymethylene-DB18C6 deposited on S (J) is greater than the same polymer without support (Table 2). The apparent reason is the high catalyst surface activity in the first case.

EXPERIMENTAL

IR spectra were recorded on a IFS-113V spectrometer in KBr. Porometric measurements were carried out in a PA-3Ml mercury porometer. The specific surface area was measured by thermal sorption and desorption of argon in a chromatographic analyzer. Thermal analysis was performed on a Q-1500D derivatograph using platinum boats, 100 mg samples, and 20 deg/min heating rate. Chromatographic analysis used a Tsvet-354 chromatograph, flame-ionization detector, 1 × 0.003 m column with 5% SE-30 on chromaton, He carrier gas (30 ml/min), source temperature 250°C, and column temperature from 120 to 220°C.

The carbonaceous material "Sibunite" [4] of 10-15 mm granule diameter was ground. The 0.16-0.20 mm fraction was sieved, washed with CHCl₃, and dried (1 torr, 80°C). UFD [5] was purified by boiling in a HNO₃/H₂SO₄ mixture, washing with 10% NaOH and water, and drying at 150°C. Silica gel (Lachema, CSSR, 0.1-0.2 mm fraction) was washed with CHCl₃ and was dried. 4',4''(5'')-di-X-dibenzo-18-crown-6 (I), (III), (VI), and IX) have been reported earlier [3, 14, 15].

Synthesis of Polymeric Crown-Ethers on Supports (cf. [1, 16]). Catalysts A-L were synthesized by refluxing a mixture of crown-ether, reagent, solvent, and support under the synthesis conditions given in Table 3. After cooling the mixture, the catalyst was filtered

off, washed on the filter with acetone and then in a Soxhlet extractor with CHCl_3 for 30 h, and dried in vacuum (1 torr, 2 h, 80°C).

Refluxing a solution of diamine (IX) in CHCl_3 without support gave a flocculent precipitate of polymeric ketimine with mp $95\text{-}105^\circ\text{C}$ (cf. [15]). Found: C, 67.02; H, 8.37%. Calculated: C, 69.81; H, 7.64%. Signals of crown moieties (see above) and C=N and CH_2 groups are seen in the IR spectrum.

Testing of Catalytic Activity. The required amount of catalyst (or 0.3 g support) was placed in a glass ampul of 15 mm diameter equipped with a glass stirrer of 9 mm blade width and 30 mm height. 1-Bromooctane (0.5 ml), chlorobenzene or decane (1.5 ml), and water (0.2 ml) were added to the ampul, which was then heated to $80 \pm 0.2^\circ\text{C}$ on a water bath. The mixture was stirred at this temperature for 1.5 h (500-700 rpm with stroboscopic monitoring) [1-3]. A saturated KI solution (1.5 ml) was added. Stirring was continued for 3 h. After cooling, the organic layer was analyzed by GLC. The catalyst was filtered off, washed with water, acetone, and CHCl_3 , and dried (1 torr, 2 h, 80°C) so that it could be used again.

LITERATURE CITED

1. A. Kh. Zitsmanis, M. K. Klyavin'sh, A. S. Roska, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 387 (1987).
2. E. Demlov and Z. Demlov, *Phase-transfer Catalysis* [Russian translation], Mir, Moscow (1987).
3. M. Hiraoka, *Crown Compounds* [Russian translation], Mir, Moscow (1986).
4. Y. I. Ermakov, V. F. Surovikin, G. V. Plaksin, et al., *React Kinet. Catal. Lett.*, **33**, 435 (1987).
5. A. I. Lyamkin, E. A. Petrov, A. P. Ershov, et al., *Dokl. Akad. Nauk SSSR*, **302**, No. 3, 611 (1988).
6. F. Svec, *Pure Appl. Chem.*, **60**, 377 (1988).
7. A. B. Zhidkov, S. K. Gordeev, E. P. Smirnov, and S. V. Novikov, *Zh. Prikl. Khim.*, (Leningrad), **57**, No. 11, 2429 (1984); All-Union Institute of Scientific and Technical Information, deposited paper No. 6912-V85 (1985).
8. A. Yu. Tsivadze, N. B. Generalova, E. Kh. Pyatova, et al., *Zh. Neorg. Khim.*, **33**, 1649 (1988).
9. Y. Gui, B. Liu, J. Liu, et al., *Youji Huaxue*, No. 5, 373 (1986).
10. P. Hodge, E. Khoshdel, and J. Waterhouse, *J. Chem. Soc. Perkin Trans. 1*, 2451 (1984).
11. S. L. Regen, *Angew. Chem. Int. Ed. Eng.*, **18**, 421 (1979).
12. A. A. Klesov and I. V. Berzin, *Enzyme Catalysis* [in Russian], *Izd. Mosk. Univ.*, Moscow (1980), pp. 12-19.
13. K. Fukunishi, B. Czech, and S. L. Regen, *J. Org. Chem.*, **46**, 1218 (1981).
14. A. K. Tashmukhamedova, I. A. Stempnevskaya, I. Yu. Morozova, and E. G. Siromenko, *Khim. Geterotsikl. Soedin.*, No. 4, 470 (1989).
15. V. F. Loktev, I. Yu. Morozova, and A. K. Tashmukhamedova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 119 (1989).
16. *Methoden der Organischen Chemie*, Vol. 14/2, Georg. Tieme Verlag, Stuttgart (1963), p. 1252.