ISSN 0965-5441, Petroleum Chemistry, 2007, Vol. 47, No. 5, pp. 331–336. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.V. Andreeva, A.L. Maksimov, A.Ya. Zhuchkova, V.V. Predeina, T.Yu. Filippova, E.A. Karakhanov, 2007, published in Neftekhimiya, 2007, Vol. 47, No. 5, pp. 362–367.

Oxidation of Unsaturated Compounds in Ionic Liquids with the Use of Cyclodextrin-Containing Catalytic Systems

L. V. Andreeva, A. L. Maksimov, A. Ya. Zhuchkova, V. V. Predeina,
T. Yu. Filippova, and E. A. Karakhanov

Moscow State University, Faculty of Chemistry, Leninskie gory, Moscow, 119899 Russia
e-mail: max@petrol.chem.msu.ru

Received January 24, 2007

Abstract—The Wacker oxidation of alkenes-1 in ionic liquids catalyzed by a system containing palladium, and copper complexes and β-cyclodextrins was studied. It was shown that the use of β-cyclodextrins substantially increases the oxidation rate in biphasic systems olefin/ionic liquid. It was found that the proposed catalytic systems possess substrate selectivity, which is determined by the structure of a receptor molecule.

DOI: 10.1134/S0965544107050039

Since the discovery of sulfonated triphenylphosphine by Kuntz, the development of new catalytic systems for reactions under biphasic conditions has become one of the most thriving lines of research in metal complex catalysis. Application of this concept assumes that metal complexes are soluble in one phase and the reactants and products are soluble in the other. Thus, a catalyst can easily be isolated from the products and recycled [1–3].

Various solvents, such as water, fluorinated hydrocarbons, and ionic liquids [3, 4–6] have been used as a phase for catalyst immobilization. The latter liquids, owing to their stability and amenability to modification, turn out to be extremely attractive for use in biphasic catalysis. However, one of problems faced upon carrying out reactions of nonpolar substrates in the presence of an ionic liquid is a low concentration of a substrate in the polar phase in which the catalyst is immobilized. Even for hexene-1, its concentration only slightly exceeds 100 mmol/l [6, 7]. As a result, reaction rates for such substrates turn out to be too low.

Earlier, by the example of aqueous-phase catalysis, it was shown that one of the general ways of solving a similar problem is the use of compounds capable of forming inclusion complexes of the host–guest type as components of catalytic systems. In this case, not only transfer of substrate to a nonpolar phase but also a change in regio- and substrate selectivity of a reaction is achieved [1–2, 8]. We have shown that macrocyclic receptors, such as calixarenes and cyclodextrins, can substantially increase the reaction rate of Wacker oxidation under biphasic conditions [9–10].

In this paper, we present the results of the study the of catalytic systems based on modified cyclodextrins in ionic liquids.

EXPERIMENTAL

In this work, β-cyclodextrin, 1-methylimidazole, tetrafluoroboric acid, and ethyl sulfate from Aldrich were used. 3-Butyl-1-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ was synthesized according to a procedure described in [11], and 1-methylimidazolium tetrafluoroborate $[HMIM]^+[BF_4]^-$ was obtained as described in [12]. 1-Methylimidazolium ethyl sulfate $[EtMIM]^+[SO_3OEt]^-$ was obtained according to the procedure [13]. Modification of β-cyclodextrin by nitrile-containing (β-CD-CN) groups was carried out by a procedure described in [1]. 2,6-Di-O-methyl-β-cyclodextrin (Met-β-CD) was prepared according to [14]. The substances were characterized by means of ^{1}H and ^{13}C NMR spectroscopy. The composition of modified cyclodextrins was additionally confirmed by the MALDI–TOF technique. The analysis was carried out on a MALDI–TOF–MS Bruker instrument (Germany). Ionization of particles was induced by an UV laser at an incident wavelength of 336 nm.

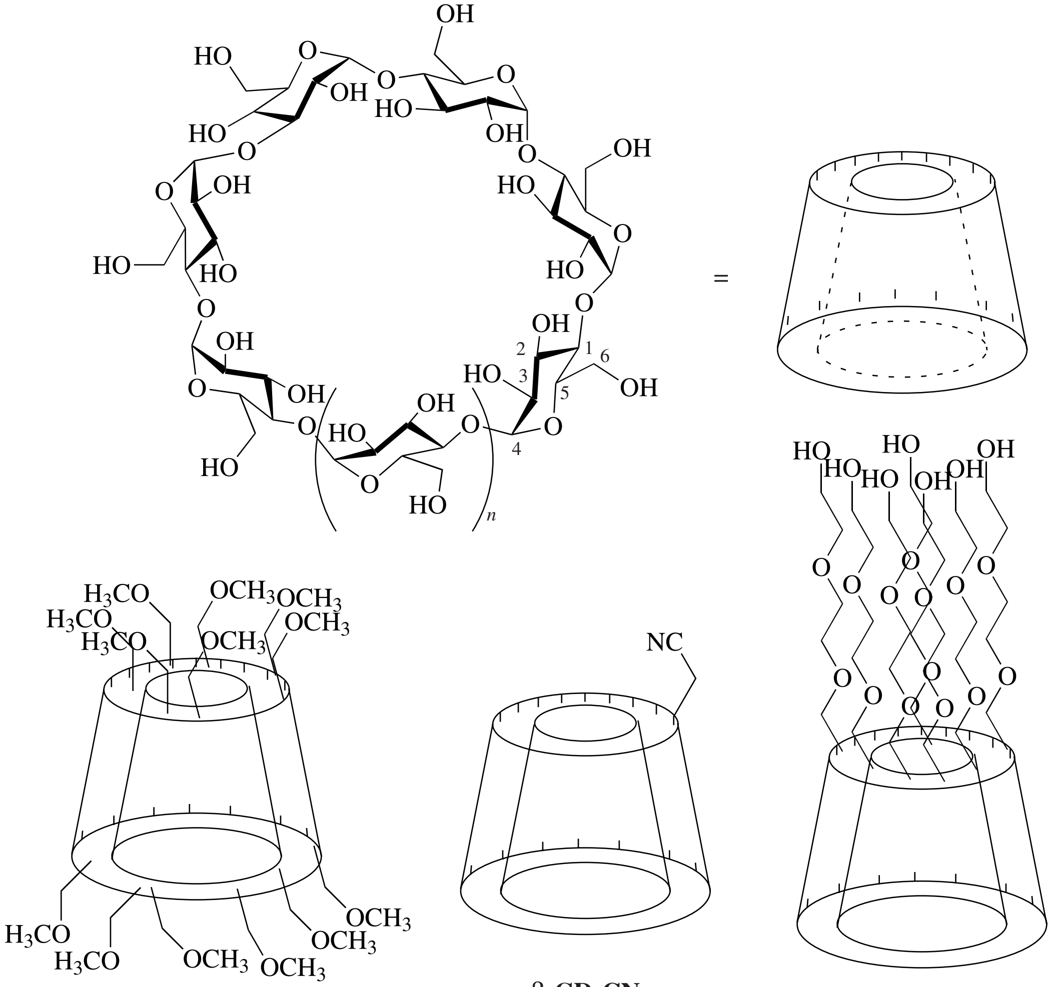
Oxyethylated β-cyclodextrin containing 28 oxyethyl fragments (β-CD-E_{28}) was synthesized as follows. A 1.135-g portion (1 mmol) of β-cyclodextrin, 0.114 g of K_2CO_3 (10 % of cyclodextrin mass) and 4.4 g (50 mmol) of ethylene carbonate were dissolved in 10 ml of tetra-*N*-methylurea. The mixture was stirred at 150°C in a nitrogen atmosphere for 4 h. After the cessation of CO_2 evolution, the solvent was distilled off, and the obtained substance was recrystallized from a 4 : 1 methanol–acetone blend. The yield of the product was 1.7 g (71%). ^{1}H NMR (δ, ppm, CD_3OD) 4.67 (H1 CD); 4.12 (H–O–C**H**$_2$CH$_2$– 3.7–3.82 (H-3, H6 CD); 3.6–3.7 (H5 CD), 3.4–3.55 (H2; H4 $-OCH_2CH_2O^-$). It was determined by the MALDI–TOF technique that from 21 up to 35 oxyethyl groups fall on one cyclodextrin molecule. The mean number of oxyethyl groups was 28. Oxyethylated cyclodextrin containing on the average five oxyethyl groups was obtained via the reaction of oxirane with cyclodextrin in an alkaline solution according to [1].

Experiments on the Wacker oxidation of octene-1, heptene-1, hexene-1, and styrene were carried out in a steel autoclave in an oxygen atmosphere at an increased pressure and a constant temperature with intense stirring of the reaction mixture. The following order of operations was maintained in the preparation of a catalytic system: the components of the catalytic system, an ionic liquid, and a substrate in quantities calculated according to desired molar ratios were loaded into a glass cartridge of the autoclave. The autoclave was tightly sealed, thermostated, and an oxygen pressure was increased to 0.5 MPa.

After completion of the experiment, the autoclave was cooled, the pressure was released, and the products were extracted with diethyl ether. The layer containing the ionic liquid was recycled for further experiments. The ethereal layer was analyzed by the GLC technique using a Chrompack CP9001 chromatograph with a flame ionization detector and a column with the SE-30 stationary phase (0.3 mm × 50 m).

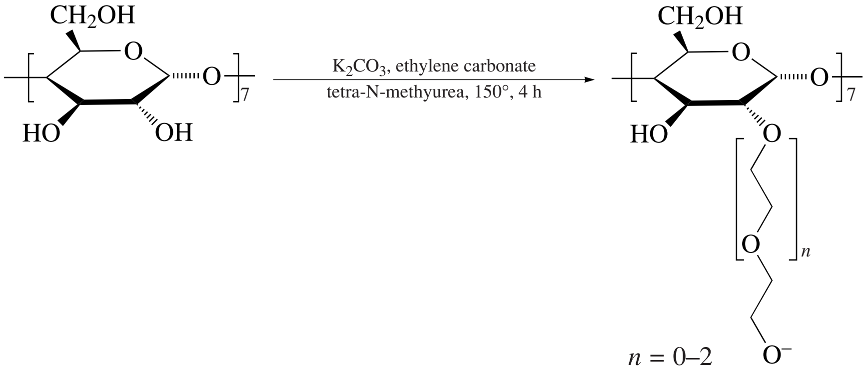
RESULTS AND DISCUSSION

As catalyst components that possess the properties of a phase-transfer agent, β-cyclodextrins modified by various oxyethyl, propionitrile, and methyl groups were chosen.



Me-βCD **β-CD-CN** **β-CD-E$_x$OH**

The modifying groups were introduced in order to increase the solubility of β-cyclodextrins in water and in ionic liquids. Cyclodextrins modified by methyl and propionitrile groups were synthesized according to the procedures described in the literature [14]. Ethoxylated cyclodextrin has been prepared under the scheme presented below:



First, we studied the oxidation of alkenes to methyl ketones in the presence of a catalyst system including palladium sulfate and copper dichloride in a solvent that comprised the water/ionic liquid system at various volume ratios of ionic liquids, a temperature of 50°C, a reaction time of 30 min, and a high stirring speed.

A high regioselectivity of the oxidation reaction is worth noting. In spite of the fact that isomeric alkenes are formed at a high rate along with oxidation, corresponding methyl ketone is the only product of oxidation. In the absence of cyclodextrins, the yield of octanone-2 increases until the volume fraction of the ionic liquid $[\mathrm{BMIM}]^+[\mathrm{BF}_4]^-$ in the solvent becomes 20 vol % (Fig. 1). The reaction rate of octene-1 oxidation increases by more than three times. With the further increase in the ionic liquid/water ratio, the yield of octanone-2 sharply decreases. This finding agrees with published data on the oxidation of alkenes-1 in ionic liquids at low oxygen pressures [15]. It seems that in this case the ionic liquid shows the properties of a hydrotrope, a compound that substantially increases the solubility of an organic compound in water owing to the formation of associates [16]. Note that such behavior is also characteristic of other reactions in an ionic liquid–polar solvent mixture [17].

It should be noted that the addition of cyclodextrin substantially increases the reaction rate in a biphasic water/alkene system, whereas the macrocyclic receptor has a substantially weaker effect on the reaction rate when an ionic liquid is added. Apparently, this phenomenon is due to the formation of inclusion complexes with molecules of the ionic liquid and with degradation of its associates. As a result of such competition, the concentration of an unsaturated compound in the aqueous phase containing an ionic liquid sharply decreases.

To run the oxidation reaction of unsaturated compounds with air oxygen in the absence of significant amounts of water, we have chosen as the catalyst a complex of $\mathrm{PdCl_2(CH_3CN)_2}$ with CuCl and HMPA, which is formed in situ in the reaction mixture in the ionic liquid $[\mathrm{BMIM}]^+[\mathrm{BF}_4]^-$ [18]. Corresponding methyl ketone and isomeric alkenes were the main products of the reaction. It should be emphasized that oxidation occurs with a high regioselectivity: isomeric ketones practically were not formed despite the formation of significant amounts of compounds with internal double bonds.

In the presence of methylated and ethoxylated β-cyclodextrin, the methyl ketone formation rate substantially increased (Fig. 2).

A similar result was obtained when the reaction was carried out in the ionic liquid $[\mathrm{Et\text{-}MIM}]^+[\mathrm{SO_3OEt}]^-$ (Table 2, Fig. 2). The growth in the oxidation rate can be explained by the formation of inclusion complexes of the host–guest type between cyclodextrin and a molecule of alkene-1, as in the case of Wacker oxidation in the biphasic water–substrate system [1–2]. In the presence of cyclodextrins, the yields of products in this case depended on the conformity of the substrate cavity to the cavity of the receptor molecule. The change was minimal for hexene-1 and maximal for heptene-1 (Fig. 2). The variation in the reaction rate also depended on the nature of a modifying group in the cyclodextrin molecule. Oxyethylated cyclodextrins displayed the maximal activity. In this case, the yield of ketone amounted to 70% for heptene-1 and more than 50% for octene-1 at 90°C already for 30 min. With an increase in the reaction temperature, the yield of products grows in the absence of cyclodextrins as well.

The employed catalytic system containing $\mathrm{PdCl_2(CH_3CN)_2}$, CuCl, HMPA, and cyclodextrins in $[\mathrm{EtMIM}]^+[\mathrm{SO_3OEt}]^-$ could be recycled in the oxidation of heptene-1 and octene-1 without the loss of activity.

The oxidation of styrenes in the absence of small amounts of water proceeded at a very low rate. The addition of 5% water resulted in a substantial increase in the reaction rate (Table 3).

Along with methyl ketone, the main products of the reaction were the corresponding aldehyde and benzaldehyde, a product of double-bond breaking, whose quantity increased with an increase in the amount of water in the system. Note that a similar result was observed by Namboodiri et al. [19] during oxidation of styrene with hydrogen peroxide in a water/ionic liquid system. When the reaction is carried out in the presence of copper dichloride, the oxidation rate increases and benzaldehyde, the product of double-bond breaking, is

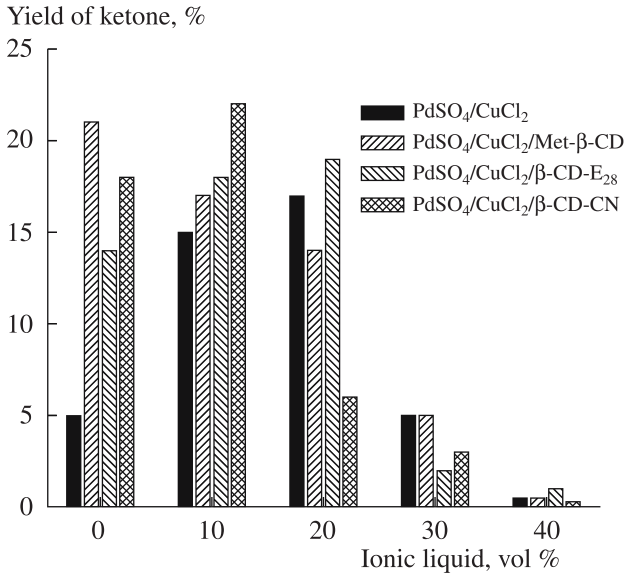


Fig. 1. Yield of octanone-2 depending on the system used. $PdSO_4 : CuCl_2 : CD : [C_8H_{16}] = 1 : 10 : 2 : 100$. Solvent, water/$[BMIM]^+[BF_4]^-$; $[C_8H_{16}] = 2$ mol/l.

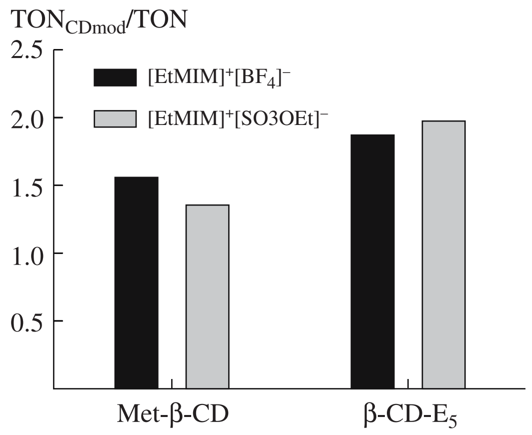


Fig. 2. Change in activity during oxidation of octene-1 to octanone-2 in the presence of various catalytic systems (O_2, 0.5 MPa; 508C, 30 min); $PdCl_2(CH_3CN)_2 : CuCl : HMPA : CD : C_8H_{18} = 1 : 1 : 2 : 0.2 : 10$; $[C_8H_{16}] = 2$ mol/l; TON is the number of moles of the product per mole of the metal in the absence of CD; and $TON_{CD\text{-}mod}$ is the number of moles of the product per mole of the metal in the presence of CD.

not formed, so that the reaction proceeds according to the mechanism traditional for the oxidation of styrene.

The use of a catalytic system containing cyclodextrins resulted in a sharp growth in the reaction rate and practically had no effect on the selectivity for reaction products. Benzaldehyde makes up about half the total quantity of the products (Fig. 3, Table 4).

In the case of styrenes, the rise in the reaction rate due to the presence of cyclodextrins in the system was substantially higher than in the case of alkenes-1. This difference can be explained in terms of high stability constants for substrates containing the aromatic moiety with cyclodextrin (Fig. 4).

Thus, we obtained results to support the concept that catalytic systems on the basis of macromolecular

Table 1. Yields of ketones-2 in the presence of the catalytic system $PdCl_2(CH_3CN)_2 : CuCl : HMPA : substrate = 1 : 1 : 2 : 10$

Substrate	Reaction time, min	Temperature, °C	
		50	90
Hexene-1	30	43%	53%
Heptene-1	30	12%	39%
	120	70%	76%
Octene-1	30	14%	40%

Table 2. Yields of ketones-2 in the presence of the catalytic system $PdCl_2(CH_3CN)_2 : CuCl : HMPA$: modified CD : substrate = 1 : 1 : 2 : 0.2 : 10 (t = 30 min)

Cyclodextrin	Substrate	Temperature, °C	
		50	90
Met-β-CD	Octene-1	19%	42%
	Heptene-1	40%	53%
β-CD-E_5	Hexene-1	34%	59%
	Heptene-1	49%	76%
	Octene-1	26%	52%
β-CD-E_{28}	Octene-1	27%	43%
	Heptene-1	50%	64%
β-CD-CN	Octene-1	23%	38%
	Heptene-1	32%	75%

Table 3. Yields of the products of the Wacker oxidation of styrene at various water contents[1]

Amount of water	Cocatalyst	Temperature, °C	Reaction time, h	Conversion, %	Selectivity, %			
					Benzaldehyde	Phenylacetaldehyde	Acetophenone	Phenylacetic acid
5%	CuCl	50	0.5	11	23	23	54	
5%	CuCl	80	2	38	36	5	29	30
10%	CuCl	80	2	56	63	7	27	3
10%	$CuCl_2$	80	2	45	–	–	76	24
10%	$CuCl_2$	80	2	53	–	–	80	20

[1] The catalyst/substrate ratio is $Pd(MeCN)_2Cl_2$: CuC1 (or $CuC1_2$) : HMPA : CD : substrate = 1 : 1 : 2 : 0.2 : 10. The total amount of the solvent is 1 ml, the concentration of the Pd(II) complex is 0.1 mmol/l, and the oxygen pressure is 5 atm.

Table 4. Selectivity in oxidation of styrenes. $PdCl_2(CH_3CN)_2$: CuCl : HMPA : CD : substrate = 1 : 1 : 2 : 0.2 : 10. [Pd(II)] = 0.1 mmol/l, 30 min. $P(O_2)$ = 0.5 MPa

Substrate		Selectivity, %		
		R–C(O)H	R–CH_2–C(O)H and R–CH_2–C(O)OH	R–C(O)–CH_3
C_6H_5–CH=CH_2 styrene	β-CDE_5	49	9	42
	–	36	35	29
CH_3–C_6H_4CH=CH_2 *p*-methylstyrene	β-CDE_5	51	35	14
	–	28	36	36
$(CH_3)_3$C–C_6H_4–CH=CH_2 *p-tert*-butylstyrene	β-CDE_5	52	2	46
	–	49	2	49

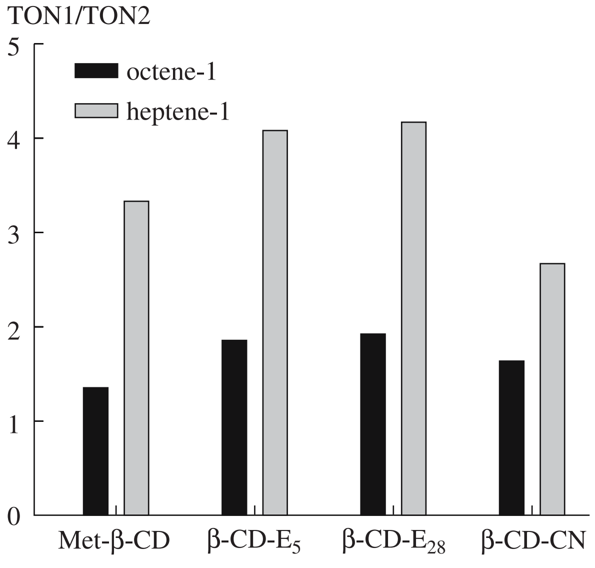


Fig. 3. Change in the reaction rate in the presence of various cyclodextrins. TON1 is the number of moles of the product per mole of the metal in the absence of CD, and TON2 is the number of moles of the product per mole of the metal in the presence of CD.

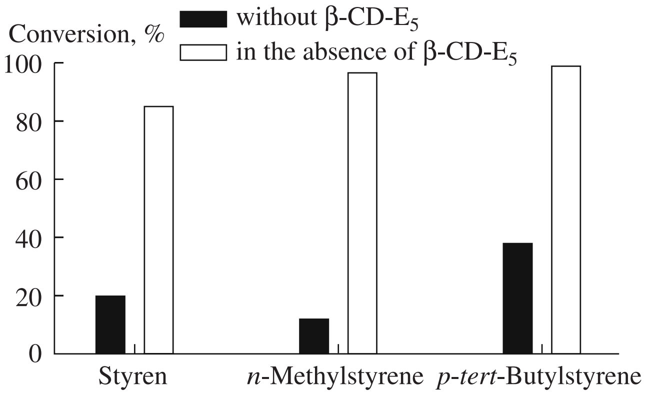


Fig. 4. Oxidation of styrenes: $PdCl_2(CH_3CN)_2$: CuCl : HMPA : CD : substrate = 1 : 1 : 2 : 0.2 : 10, [Pd(II)] = 0.1 mmol/l, 30 min, $P(O_2)$ = 0.5 MPa.

receptors have considerable promise for carrying out reactions with nonpolar substrates in ionic liquids.

ACKNOWLEDGEMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-03-32889a.

REFERENCES

1. E. A. Karakhanov, A. L. Maximov, T. Yu. Filippova, et al., Polym. Adv. Technol. **12**, 161 (2001).
2. E. Karakhanov and A. Maximov, in *Metal Complexes and Metals in Macromolecules*, Ed. by D. Wohrle and A. Pomogajlo (Wiley–VCH, 2003), p. 457.
3. B. Cornils and H. Hermann, *Aqueous Phase Organometallic Catalysis: Concepts and Applications*, (Wiley, Weinheim 1998).
4. E. Karakhanov, A. Maximov, E. Runova, et al., Macromol. Symp. **204**, 159 (2003).
5. B. Cornils, Angew. Chem., Int. Ed. Engl. **36**, 2057 (1997).
6. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, (Wiley–VCH, 2003).
7. F. Favre, H. Olivier-Bourbigou, D. Commereuc, and L. Saussine, Chem. Commun., 1360 (2001).
8. A. L. Maksimov, T. S. Buchneva, and E. A. Karakhanov, J. Mol. Catal. A, **217**, 59 (2004).
9. E. A. Karakhanov, A. Ya. Zhuchkova, A. L. Maksimov, et al., Neftekhimiya **42**, 233 (2002) [Pet. Chem. **42**, 181 (2002)].
10. E. A. Karakhanov, A. Ya. Zhuchkova, T. Yu. Filippova, and A. L. Maksimov, Neftekhimiya **43**, 302 (2003) [Pet. Chem. **43**, 273 (2003)].
11. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem. **21**, 1263 (1982).
12. J. D. Holbrey and F. R. Seddon, J. Chem. Soc., Dalton Trans., 2133 (1999).
13. J. D. Holbrey, W. M. Reichert, R. P. Swatloski, and G. A. Broker, Green Chem. **4**, 407 (2002).
14. US Patent No. 5 008 386 (1991).
15. I. A. Ansaria, Sipak Joyasawala, K. Manoj, et al., Tetrahedron Lett. **46**, 7507 (2005).
16. V. F. Sergeeva, Usp. Khim. **34** (4), 717 (1965).
17. F. D’Anna, V. Frenna, V. Pace, and R. Noto, Tetrahedron **62**, 1690.
18. T. Hosokawa, S. Aoki, M. Takano, et al., Chem. Commun., 1559 (1991).
19. V. V. Namboodiri, R. S. Varma, E. Sahle-Demessie, and U. R. Pillai, Green Chem. **4**, 170 (2002).