Phosgene-free synthesis of carbamates over zeolite-based catalysts

R. Srivastava, M.D. Manju, D. Srinivas*, and P. Ratnasamy**

National Chemical Laboratory, Pune 411 008, India

Received 22 April 2004; accepted 14 May 2004

Alkyl and aryl carbamates are synthesized in high yields (≥80%) at mild reaction conditions by reaction of the corresponding amine, CO_2 and alkyl halides over either titanosilicate molecular sieves or metal phthalocyanine complexes encapsulated in zeolite-Y. The catalysts could be reused with little or no loss in activity. In contrast to hitherto known catalysts for carbamate synthesis, the zeolite-based catalysts of the present study do not require additional onium salts as co-catalysts.

KEY WORDS: carbamates; urethanes; phosgene-free synthesis; carbon dioxide utilization; titanosilicates; zeolite-encapsulated metal complexes; metal phthalocyanines; TS-1; Ti-MCM-41; Ti-SBA-15.

1. Introduction

Carbamates (ROCONHR′; R and R′ = alkyl or aryl) are important raw materials for the manufacture of a variety of polymers (e.g., polyurethanes) used in foams, coating, adhesives, plastics and fibers. They are also used as herbicides, fungicides and pesticides in agrochemical industry (e.g., carbaryl, carbofuran, propoxur, dioxacarb, aminocarb etc.) and drug intermediates in pharmaceutical industry (e.g., secondary amyl carbamate, trichloroethyl carbamate, physostigmine, carbachol etc.) [1–5]. The commercial production of carbamates is almost exclusively based on the phosgene/isocyanate technology (scheme 1) [1]. The phosgene/isocyanate processes inherently involve a number of environmental and safety shortcomings (e.g., the Bhopal disaster of 1984 in a methyl isocyanate plant). A further incentive to eliminate phosgene is the economic penalty incurred because the chlorine content of the phosgene is wasted and converted to NaCl. Caustic soda is consumed in the conversion and the disposal of waste salt solutions presents ecological problems in itself. Two phosgene-free alternate approaches including: (1) the reductive carbonylation of nitro aromatics and (2) oxidative carbonylation of amines have been proposed (scheme 1) [6–16]. However, the reductive carbonylation route (using platinum group metal catalysts) is economically not viable; only one-third of CO could be utilized effectively and the separation of CO from CO_2 increases the operation cost. Most importantly, the presence of redox-active co-catalysts (ferrous chlorides) results in corrosion problems and makes recovery of the catalyst difficult. The second oxidative carbonylation route involving the handling of hazardous (CO + O_2) mixtures at harsh conditions (50–400 bar; 443 K) is also not satisfactory. Carbamates can also be synthesized by the Hoffmann rearrangement of amides, reaction of chloroformates and amines, methoxycarbonylation of amines etc. (scheme 2) [17–19]. In the last mentioned process dimethyl carbonate (DMC) is used as a methoxy carbonylating agent. Separation of the methanol–DMC azeotrope is, however, an expensive operation in this process.

The reaction of CO_2 with a primary amine yields the carbamate anion [20–27]. Reaction of this anion with various alkyl halides can yield the corresponding carbamates (scheme 3). Strong organic bases, crown ethers and onium salts have been found to stabilize the carbamate anion [28–32]. In addition, ionic liquids and solids such as $CsCO_3$ and K_2CO_3 have also recently been claimed to catalyze the carbamate synthesis through the anion route [33–35]. However, due to their low activity very large quantities of such catalysts (almost equal to the quantity of substrates) had to be used at long reaction times (24 h) and large amounts of alkyl halide [28–32]. Hence, there still exists a need for an efficient solid catalyst for the phosgene-free synthesis of carbamates.

We have now found that titanosilicate molecular sieves and metal phthalocyanine complexes encapsulated in zeolite-Y are superior catalysts for carbamate synthesis by a phosgene/isocyanate/CO-free route from a broad range of amine substrates, CO_2 and alkyl halide. High carbamate yields (≥80%) could be achieved at mild optimized reaction conditions (353 K and 3.4 bar). The catalysts are recyclable. A novel application of these catalyst systems in the synthesis of polycarbonate precursors by a phosgene/CO-free route involving

*To whom correspondence should be addressed.
E-mail: srinivas@cata.ncl.res.in
**To whom correspondence should be addressed.
E-mail: prs@ems.ncl.res.in

1011-372X/04/0800–0041/0

(a) Phosgene route - Amination of alkylchloroformate:

$$ROH + COCl_2 \longrightarrow ROCOCl + HCl$$

$$ROCOCl + 2NH_3 \longrightarrow ROCONH_2 + NH_4Cl$$

(b) Phosgene/Isocyanate route:

$$R'NH_2 + COCl_2 \longrightarrow R'NCO + 2\,HCl$$

$$R'NCO + ROH \longrightarrow R'NHCOOR$$

(c) Reductive carbonylation of nitro aromatics:

$$R'NO_2 + 3\,CO + ROH \longrightarrow R'NHCOOR + 2\,CO_2$$

(d) Oxidative carbonylation of amines:

$$R'NH_2 + CO + O_2 + ROH \longrightarrow R'NHCOOR + H_2O$$

Scheme 1.

(a) Hoffmann rearrangement of amides:

$$ROCONH_2 + R'OH \longrightarrow R'NHCOOR$$

(b) Reaction of chloroformates and amines:

$$R'NH_2 + Cl(CO)OR \longrightarrow R'NHCOOR$$

(C) Methoxy carbonylation of amines:

$$R'NH_2 + ROCOOR \longrightarrow R'NHCOOR + ROH$$

Scheme 2.

$$2\,R'NH_2 + CO_2 \rightleftharpoons [R'NHCOO^-][R'NH_3^+]$$

$$[R'NHCOO^-][R'NH_3^+] + RX \longrightarrow R'NHCOOR + R'NH_2 + HX$$

Scheme 3.

olefins, H_2O_2 and CO_2 was reported by us earlier [36,37]. In the present paper we extend their application to the synthesis of carbamates.

2. Experimental

2.1. Materials

Preparation of Titanosilicates. TS-1 (Si/Ti = 36 (XRF); BET surface area = 400 m^2/g) and TiMCM-41 (Si/Ti = 46 (XRF); BET surface area = 963 m^2/g; pore volume = 0.9 cm^3 and pore diameter = 30 Å) were prepared and characterized as reported earlier [36]. SBA-15 was prepared as per the procedure given in reference [38]. Ti-SBA-15 (Si/Ti = 30 (XRF); BET surface area = 790 m^2/g, pore volume = 1.7 cm^3 and pore diameter = 83 Å) was prepared by a post synthesis method using tetrabutyl orthotitanate (TBOT) as the Ti source [38]. Amorphous TiO_2–SiO_2 (Si/Ti = 37; S_{BET} = 273 m^2/g) was prepared [39] from a gel of molar composition: tetraethyl orthosilicate (TEOS) : 0.55 cetyl trimethyl ammonium bromide (CTMABr) : 0.33 tetramethyl ammonium hydroxide (TMAOH) : 0.0303 TBOT : 60 H_2O.

Purity and crystallinity of the samples were confirmed by XRD. Isolation and framework substitution of Ti^{4+} ions (in the case of TS-1) was established using diffuse reflectance UV–visible (208, 224, 216 and 208 nm for TS-1, Ti-MCM-41, Ti-SBA-15 and TiO_2–SiO_2, respectively) and FT-IR (968 and 964 cm^{-1} for TS-1 and Ti-MCM-41, respectively) spectroscopies. Anatase, TiO_2 was absent as confirmed by the absence of the 330 nm UV band. All the substrates and solvents were obtained from s. d. fine chem. Ltd, Mumbai.

Preparation of MPc-Y. The zeolite-Y-encapsulated metal phthalocyanine complexes (MPc-Y, M = Cu, Co, Ni and Al) were prepared by the "*in situ* ligand synthesis" method using metal ion-exchanged Y and 1,2-dicyanobenzene (DCB) [37]. The metal ion content was estimated by atomic absorption spectroscopy (AAS) to be Cu, 0.41 wt%, Co, 0.58 wt%, Ni, 0.29%, respectively.

2.2. Characterization techniques

The chemical composition was estimated using a Rigaku 3070 E wavelength dispersive XRF spectrometer with a Rh target energized at 50 kV and 40 mA. The X-ray diffractograms of calcined titanosilicates were recorded on Rigaku Miniflex and SAXS diffractometers. The surface area and pore volume parameters were determined from N_2 adsorption isotherms obtained using a Coulter 100 instrument. The FT-IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the region 400–4000 cm^{-1}. The diffuse reflectance UV–visible spectra were measured on a Shimadzu UV-2550 spectrophotometer in the region 200–800 nm.

2.3. Reaction procedure and product identification

In a typical reaction, an amine like aniline (2 mmol), alkyl halide like *n*-butyl bromide or chloride (1–6 mmol), solvent (CH_3OH, CH_3CN, *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMA) or *N*-methyl-2-pyrolidone (NMP); 10 g) and catalyst (titanosilicate molecular sieves, 100 mg or MPc-Y, 83 mg) were charged to a 300 mL stainless steel Parr reactor. The reactor was then pressurized with CO_2 (3.4 bar). Temperature was raised to the desired value (323–353 K) and reactions were conducted for 3 h. The reactor was then cooled to 298 K and unutilized CO_2 was vented out. The catalyst was recovered from the reaction mixture by filtration.

The filtrate was poured into water (30 mL) and extracted with ethyl acetate (30 mL, 3 times). The organic layer was washed with water (30 mL, 2 times) and brine

(30 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated. The products were analyzed by thin layer chromatography (TLC) and gas chromatography (Shimadzu 14B GC; SE-52 packed column (6-feet long × 1.25-mm i.d.)). They were characterized and identified by GC-MS (Shimadzu QP-5000 (30-m long × 0.25-mm i.d.)), FT-IR (Shimadzu 8201 PC spectrophotometer) and ^{1}H NMR (Bruker AC 200) spectroscopies. Mass balances were routinely carried out (>98%). In some cases the products were isolated by column chromatography (silica gel 60–120 mesh; 98 : 2 petroleum ether : ethyl acetate mixture as eluent) and yields were estimated.

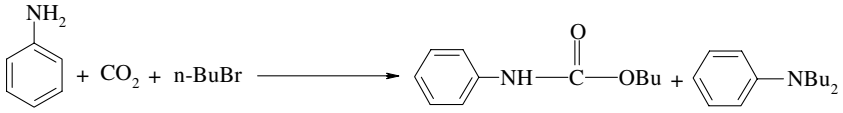
Experiments were also performed without any solvent. A range of carbamates were synthesized and characterized in a similar manner as described above.

3. Results and discussion

3.1. Catalytic activity of titanosilicates

The reaction of aniline, CO_2 and *n*-butyl halide yielded two products, butyl-*N*-phenyl carbamate as the major product and *N*,*N*-dibutylaniline (*N*-alkylation) as the minor product (scheme 4). The products were isolated by column chromatography and identified by GC-MS, FT-IR and ^{1}H NMR spectroscopies. Butyl-*N*-phenyl carbamate was confirmed by FT-IR peaks at 3053 and 3392 cm^{-1} due to N–H stretching vibration, 1728 and 1242 cm^{-1} due to anti-symmetric and symmetric O=C—O vibrations and 1040 cm^{-1} due to Bu–O stretching vibrations, respectively. *N*,*N*-dibutylaniline was characterized by peaks at 921 and 652 cm^{-1} due to (Bu)C—N—C(Bu) bending/deformations. In the ^{1}H NMR spectra of the products, due to the absence of electron withdrawing carbamate group, ^{1}H resonances at around 7.3, 6.3δ (phenyl), 3.5, 1.75, 1.5δ (methylene of Bu) and 0.9δ (methyl of Bu) (in carbamate) are all upfield shifted to (6.7, 6.3), 2.7, 1.3, 0.9, 0.6δ, respectively in *N*,*N*-dibutylaniline. The integrated proton intensities agreed well with the molecular structure (mass spectroscopy).

Even though the reaction proceeds in the absence of a catalyst, aniline conversions were lower (26.2% in DMF, 5.9% in CH_3OH and 3.9% in CH_3CN; the higher conversions in DMF are probably due to the higher solubility of CO_2 in this solvent.) (tables 1 and 2). With aniline as substrate, no marked difference in catalytic activity was observed over different titanosilicate catalysts (table 1; Run numbers 2–5). Solvents influence, significantly, the catalytic activity and product selectivity (table 2); aniline conversion over TS-1 catalyst increases in the order: CH_3CN (44.6%) ≈ CH_3OH (45.5%) < DMF (95.8 wt%). Carbamate selectivity is, however, lower in DMF (59.4%) than in CH_3CN and CH_3OH (~90%). The reaction occurs even in the absence of any solvent but *N*,*N*-dibutylaniline (*N*-alkylated product) is formed in higher amounts (64%) than the carbamate (36%). While conversion increased with temperature, selectivity to the carbamate decreased (88–59.4%) (table 2). Carbamate selectivity decreased also at high alkyl halide concentrations (table 3). High carbamate yields are obtained at low *n*-alkyl halide concentration (*n*-BuBr/aniline = 0.5 mol/mol), in the DMF solvent and at temperatures in the range 343–353 K.



Scheme 4.

Table 1
Synthesis of butyl-*N*-phenyl carbamate over titanosilicate molecular sieves[a]

Run number	Catalyst	Si/Ti	Aniline conversion (wt%)	TOF (h^{-1})[b]	Product selectivity (wt%)	
					Butyl-*N*-phenyl carbamate	*N*, *N*-Dibutylaniline
1	Nil	–	26.2	–	96.8	3.2
2	TS-1	36	81.6	12	82.9	17.1
3	Ti-MCM-41	46	63.1	12	85.6	14.1
4	Ti-SBA-15	30	78.1	9	82.5	17.5
5	Amorphous TiO_2–SiO_2	37	74.4	11	82.4	17.6

[a]Reaction conditions: aniline, 2 mmol; *n*-BuBr, 2 mmol; CO_2, 3.4 bar; DMF, 10 g; catalyst, 100 mg; temperature, 353 K; run time, 3 h. Run number. 1 was performed with no catalyst.
[b]TOF = moles of aniline converted per mole of Ti per hour.

Table 2
Influence of temperature and solvent on the synthesis of butyl-*N*-phenyl carbamate over TS-1[a]

Run number	Temperature (K)	Solvent	Conversion (wt%)	TOF (h^{-1})[b]	Product selectivity (wt%)	
					Butyl-*N*-phenyl carbamate	*N*, *N*-Dibutylaniline
1	353	CH_3CN	44.6	6	89.2	10.8
2[c]	353	CH_3CN	3.9	–	100	0
3	353	CH_3OH	45.5	6	89.7	10.3
4[c]	353	CH_3OH	5.9	–	96.0	4.0
5	353	DMF	95.8	14	59.4	40.6
6[c]	353	DMF	26.2	–	96.8	3.2
7	343	DMF	80.6	12	76.9	23.1
8	333	DMF	70.1	10	88.0	12.0
9	323	DMF	47.0	7	88.0	12.0
10	353	No solvent	89.4	13	36.0	64.0

[a]Reaction conditions: aniline, 2 mmol; *n*-BuBr, 6 mmol; CO_2, 3.4 bar; solvent, 10 g; catalyst, 100 mg; run time, 3 h.
[b]TOF = moles of aniline converted per mole of Ti per hour.
[c]Run numbers 2, 4 and 6 were performed with no catalyst.

Table 3
Influence of alkyl halide concentration on the catalytic activity[a]

Concentration of *n*-BuBr (mmol)	Conversion (wt%)	TOF (h^{-1})[b]	Product selectivity (wt%)	
			Butyl-*N*-phenyl carbamate	*N*,*N*-Dibutylaniline
1.0	46.5	7	96.0	4.0
1.5	53.0	8	92.3	7.7
2.0	81.6	12	82.9	17.1
3.0	82.4	12	78.2	21.8
4.0	91.4	13	77.7	22.3
6.0	95.8	14	59.4	40.6

[a]Reaction conditions: aniline, 2 mmol; CO_2, 3.4 bar; DMF, 10 g; TS-1, 100 mg; temperature, 353 K; run time, 3 h.
[b]TOF = moles of aniline converted per mole of Ti per hour.

A broad range of amines could be converted to carbamates by this method (table 4). Carbamate yields decreased in the order: *n*-dodecylamine (89.5%) ≈ aniline (89.3%) ≈ hexylamine (89.4%) > benzylamine (63.4%) > cyclohexylamine (58.7%) > 2,4,6-trimethylaniline (54.7%) > cyclododecylamine (8.1%). In the case of bulky substrates like 2,4,6-trimethylaniline and cyclododecylamine, the mesoporous Ti-SBA-15 was more active than the medium-pore TS-1 (table 4).

Table 4
Carbamate synthesis – influence of substrate[a]

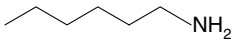
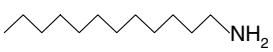
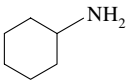
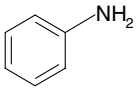
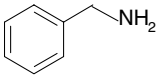
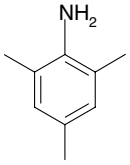
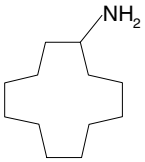
Amine	Titanosilicate	Alkyl halide	Amine conversion (wt%)	TOF (h^{-1})[b]	% Product selectivity		Carbamate yield%
					Carbamate	*N*-Alkylated product	
	TS-1	*n*-BuBr	91.4	13	94.5	5.5	86.4
	TS-1	*n*-BuCl	83.0	12	96.4	3.6	80.0
	TS-1	*n*-BuBr	92.8	13	96.5	3.5	89.5
	TS-1	*n*-BuCl	78.4	11	95.2	4.8	74.6
	TS-1	*n*-BuBr	63.2	9	92.5	7.5	58.5
	TS-1	*n*-BuCl	53.8	8	96.4	3.6	51.9

Table 4
Continued[a]

Amine	Titanosilicate	Alkyl halide	Amine conversion (wt%)	TOF (h^{-1})[b]	% Product selectivity		Carbamate yield%
					Carbamate	*N*-Alkylated product	
	TS-1	*n*-BuBr	93.0 (94.2)[c]	13 (13)[c]	96.0 (96.1)[c]	4.0 (3.9)[c]	89.3 (90.5)[c]
	TS-1	*n*-BuCl	81.4	12	96.7	3.3	78.7
	TS-1	*n*-BuBr	66.6	10	95.2	4.8	63.4
	TS-1	*n*-BuCl	60.4	9	87.6	12.4	52.9
	TS-1	*n*-BuBr	56.0	8	97.8	2.2	54.7
	Ti-SBA-15	*n*-BuBr	76.0	9	97.1	2.9	73.8
	TS-1	*n*-BuBr	8.6	1	93.8	6.2	8.1
	Ti-SBA-15	*n*-BuBr	27.4	3	88.4	11.6	24.2

[a]Reaction conditions: amine, 2 mmol; *n*-Bu*X*, 1 mmol; TS-1, 100 mg; DMF, 10 g; CO_2, 3.4 bar; temperature, 353 K; run time, 3 h.
[b]TOF = moles of substrate converted per mole of Ti per hour.
[c]Values in parentheses are those obtained on recycle of the catalyst.

3.2. Catalytic activity of metal phthalocyanines encapsulated in zeolite-Y (MPc-Y)

Carbamate synthesis over MPc-Y catalysts is reported in table 5. The intrinsic activity (TOF) decreased in the order: NiPc-Y (TOF = 135) > CuPc-Y (107) > "neat" CuPc (85) > CoPc-Y (72). The MPc-Y catalysts could be easily separated and recycled with negligible loss in activity (table 5). The superior activity of the CuPc-Y compared to the "neat" CuPc complex is attributed to the geometric distortion of the isolated MPc molecules in the supercages of zeolite-Y and consequent electronic changes (REF). Higher carbamate selectivites (92%) could be achieved when lower amounts of alkyl halides are used (table 5). The carbamate yields in different solvents over CuPc-Y decreased in the order: *N*,*N*-dimethyl formamide (DMF) > NMP > *N*,*N*-dimethylacetamide (DMA) > CH_3OH > CH_3CN (table 6).

Table 5
Synthesis of butyl-*N*-phenyl carbamate over zeolite-Y-encapsulated metal phthalocyanine complexes (MPc-Y)[a]

MPc-Y	Aniline conversion (wt %)	TOF h^{-1}	Product selectivity (%)[e]	
			A	*B*
CuPc-Y	86.1	107	79.6	20.4
CuPc-Y[b]	59.4	74	92.6	7.4
NiPc-Y	83.3	135	78.7	21.3
CoPc-Y	89.2	72	74.8	25.2
CoPc-Y- I[c]	91.5	74	70.2	29.8
CoPc-Y – II[d]	92.9	75	69.8	30.2
CuPc- "neat"	93.1	85	71.0	29.0

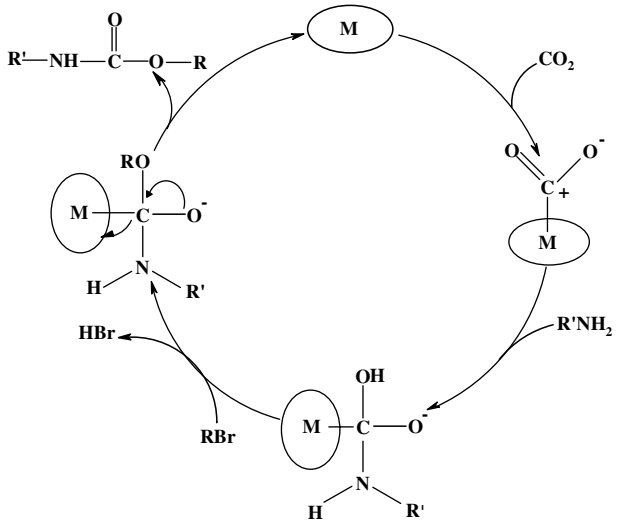
[a]Reaction conditions: catalyst (83 mg for MPc-Y and 0.0072 mmol for CuPc-"neat"), aniline (2 mmol), CO_2 (3.4 bar), *n*-BuBr (6 mmol.), DMF (10 g), temperature (80 °C), reaction time (3 h).
[b]*n*-BuBr 2 mmol instead of 6 mmol was used.
[c]1st Recycle.
[d]2nd Recycle.
[e]Products: A – butyl-*N*-phenyl carbamate. B – *N*,*N*-Dibutylaniline.

Table 6
Influence of solvent on the syntheis of butyl-*N*-phenyl carbamate over CuPc-Y[a]

Solvent	Aniline conversion (wt%)	Product selectivity (mol %)[b]	
		A	B
No solvent	99.1	41.4	58.6
CH_3CN	46.0	92.4	7.6
CH_3OH	61.6	85.4	14.6
DMF	93.6	80.0	20.0
NMP	98.2	64.0	36.0
DMA	94.4	64.1	35.9

[a] Reaction conditions: CuPc-Y (83 mg), aniline (2 mmol), CO_2 (3.4 bar), *n*-BuBr (6 mmol), DMF (10 g), temperature (80 °C), reaction time (3 h).
[b] Products: A – Butyl-N-phenyl carbamate; B – N, N-dibutylaniline.

Over other solid catalysts, like $CsCO_3$ [33–35], onium salts like tetrabutylammonium bromide and iodide have to be used as co-catalysts to stabilize the carbamate anion and avert direct *N*-alkylation and alkylation of the product carbamate. Recovery/recycle/disposal of such onium salts poses environmental and economic challenges. With the present catalysts, however, the carbamate anion is stabilized by the zeolite itself, requiring no additional co-catalyst. A tentative reaction scheme for carbamate synthesis over MPc catalysts is shown in scheme 5.



Scheme 5.

4. Conclusions

Carbamates are synthesized in high yields via a phosgene/isocyanate/CO-free route using either titanosilicate molecular sieves or metal phthalocyanine complexes encapsulated in zeolite-Y. Solvent, temperature and alkyl halide influence the carbamate yield. At optimal conditions aniline conversion and carbamate selectivities greater than 80% could be achieved. Unlike earlier phosgene-free processes, no additional co-catalysts such as organic bases, crown ether or onium salts are needed when these zeolite catalysts are used. Our novel zeolite-based process not only overcomes the environmental and economic problems of the current phosgene/isocyanate/CO processes but also contributes to the earths environment through CO_2 utilization.

Acknowledgment

This work is funded by the Council of Scientific and Industrial Research (CSIR), New Delhi in form of a sponsored network project (''Catalysis and Catalysts'', P23-CMM0005-D). R.S. acknowledges CSIR, New Delhi for a Research Fellowship.

References

[1] *An Ullmann Encyclopedia: Industrial Organic Chemicals: Starting Materials and Intermediates*, Vol. 2 (Wiley–VCH, New York, 1999) p. 1045.
[2] D.B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti and G. Pampaloni, Chem. Rev. 103 (2003) 3857.
[3] F. Paul, Coord. Chem. Rev. 203 (2000) 269.
[4] M. Aresta and E. Quaranta, Chem. Tech. 3 (1997) 32.
[5] T.W. Greene and P.G.M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed. (John Wiley and Sons, Inc., New York, 1991) p. 315.
[6] T. Takeuchi, M. Nishi, T. Irie and H. Ryuto, US Patent 4,469,882 (1984).
[7] E. Drent, L. Van and W.N.M. Petrus, US Patent 4,474,978 (1984).
[8] T.W. Leung and B.D. Dombek, US Patent 5,194,660 (1993).
[9] R.V. Chaudhari, S.P. Gupte, A.A. Kelkar and D.S. Kolhe, US Patent 5,502,241 (1996).
[10] F. Ragini, S. Cenini and F. Demartin, J. Chem. Soc. Chem. Commun. (1992) 1467.
[11] F. Ragini and S. Cenini, J. Mol. Catal. A: Chem. 109 (1996) 1.
[12] S. Fukuoka, M. Chono and M. Kohno, J. Org. Chem 49 (1984) 1458.
[13] S.T. Gupte and R.V. Chaudhari, J. Catal. 214 (1998) 246.
[14] K.T. Li and Y.J. Peng, J. Catal. 143 (1993) 631.
[15] B. Chen and S.S.C. Chuang, J. Mol. Catal. A: Chem. 195 (2003) 37.
[16] F. Shi, Y. Deng, T. Sima and H. Yang, J. Catal. 203 (2001) 525.
[17] Y. Matsumura, T. Maki and Y. Satoh, Tetrahedron Lett. 38 (1997) 8878.
[18] J.S. Yadav, G. Reddy, M. Reddy and H. Meshram, Tetrahedron Lett. 39 (1998) 3259.
[19] P. Koèovský, Tetrahedron Lett. 27 (1986) 5521.
[20] W.D. MacGhee, Y. Pan and D.P. Riley, J. Chem. Soc., Chem. Commun. (1994) 699.
[21] M. Aresta and E. Quaranta, Tetrahedron 48 (1992) 1515.
[22] B.H. Lee, US Patent 6,528,678 (2003).
[23] K.W. Jung, US Patent 6,399,808 (2002).
[24] D. Chaturvedi, A. Kumar and S. Ray, Synth. Commun. 32 (2002) 2651.
[25] D. Chaturvedi, A. Kumar and S. Ray, Tetrahedron Lett. 44 (2003) 7637.
[26] E.R. Perez, M.O. da Silva, V.C. Costa, U.P. Rodrigues and D.W. Franco, Tetrahedron Lett. 43 (2002) 4091.
[27] R.N. Salvatore, S.I. Shin, A.S. Nagle and K.W. Jung, J. Org. Chem. 66 (2001) 1035.
[28] A. Inesi, V. Mucciante and L. Rossi J. Org. Chem. 63 (1998) 1337.
[29] M. Yoshida, N. Hara and S. Okuyama, J. Chem. Soc., Chem. Commu. (2000) 151.
[30] F. Shi, J. Peng and Y. Deng, J. Catal. 219 (2003) 372.
[31] T. Sima, S. Guo, F. Shi and Y. Deng, Tetrahedron Lett. 43 (2002) 8145.
[32] W. McGhee, D. Riley, K. Christ, Y. Pan and B. Parnas, J. Org. Chem. 60 (1995) 2820.
[33] I. Vauthey, F. Valot, C. Gozzi, F. Fache and M. Lamaire, Tetrahedron Lett. 41 (2000) 6347.
[34] F. Shi and Y. Deng, J. Catal. 211 (2002) 548.
[35] A. Wolf and F. Schüth, Appl. Catal. A 226 (2002) 1.

[36] R. Srivastava, D. Srinivas and P. Ratnasamy, Catal. Lett. 91 (2003) 133.
[37] R. Srivastava, D. Srinivas and P. Ratnasamy, Catal. Lett. 89 (2003) 81.
[38] P. Wu, T. Tatsumi, T. Komatsu and T. Yashima, Chem. Mater. 14 (2002) 1657.
[39] R. Srivastava, D. Srinivas and P. Ratnasamy, Catal. Today (2004) (in press).