JOURNAL OF CATALYSIS **176,** 305–309 (1998)
ARTICLE NO. CA982055

Selective Dihydroxylation over Titanium Silicate Molecular Sieves

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Received September 2, 1997; revised January 30, 1998; accepted February 23, 1998

Titanium silicate molecular sieve, TS-1, has been found to be a highly efficient and selective catalyst in dihydroxylation of olefins under triphase reaction conditions in the presence of dilute hydrogen peroxide. Among the substrates unsaturated alcohols ($\geqq C_4$) give selectively corresponding triol in a very high yield with very high H_2O_2 efficiency. Unsaturated halides give the corresponding diols even at a faster reaction rate. Whereas under the conventional biphase system (in the presence of a cosolvent to homogenize the liquid layers) epoxide is obtained as the major final product in high yield. The substrate nature, i.e., steric hindrance at the active site and hydrophobicity/hydrophilicity of both substrate and epoxide intermediate, is considered to account for the product distribution. Acidity generated *in situ* over TS-1 in the presence of water (used as the dispersion medium) is responsible for the bifunctional (oxidation and acidic) behavior of the titanium silicate.

INTRODUCTION

Dihydroxylation reaction is of great interest in synthetic organic chemistry not only because of its utility in the formation of the primary building units to construct various carbohydrates but because of its possibility to lead to asymmetric synthesis (1, 2) through appropriate reaction conditions. Titanium silicates, mainly TS-1 (3) (MFI topology), have been extensively used in various selective oxidation reactions over the last decade. As far as the oxidation of olefins over titanium silicate is concerned, epoxide is known to be the predominant product in the presence of dilute hydrogen peroxide (4, 5). Much attention has been paid to the enhancement of the epoxide yield, together with minimization of diols, by-products of this reaction, because of the industrial interest in the production of pure epoxide. On the other hand, diols are synthesized mainly via syn addition of OsO_4 (6), MnO_4^- (7), or chromyl chloride (8) to olefins or anti-acid or base-catalyzed hydrolysis of epoxides (9, 10) under strong and unrecyclable conditions; selective ring opening of the epoxides (11, 12) by protic molecules is also an important methodology for the synthesis of diols. The chemical industry requires high yield, high selectivity, sufficient productivity, low cost, safety, operational simplicity and environmental consciousness, among other technical factors. Here we report direct dihydroxylation of relatively hydrophobic olefins under recently developed triphase condition (13) in an eco-friendly way (in the absence of hazardous organic cosolvents). Product diols and triols thus formed in high yield are valuable intermediates in the production of speciality chemicals such as pharmaceuticals. Apart from chemoselective dihydroxylation at the olefinic double bond, present methodology offers the distinct advantage of easier workup. Factors responsible for high reactivity and high diol selectivity, along with a plausible mechanism are described in detail.

EXPERIMENTAL

TS-1 (Si/Ti = 27) used in the present study is synthesized by the standard literature procedure (12). Samples are thoroughly characterized by XRD, UV-Vis, FT IR spectroscopy, which ascertained that those are free from crystalline and amorphous impurities. This highly crystalline TS-1 material is composed of uniform cuboid crystals of 0.2–0.25 μm size as revealed by a scanning electron microscopy. Liquid phase batch reactions are carried out in a three-necked glass reactor fitted with water condenser under inert nitrogen atmosphere at 333 K. Solid catalyst, organic substrate, and aqueous phase consisting of dilute hydrogen peroxide constitutes three distinct phases. In a typical reaction 1.72 g of *cis*-2-pentene-1-ol was taken with 2.26 g of dilute hydrogen peroxide (30% aqueous) and to it 10 g of H_2O and 0.35 g of TS-1 was added. The reaction was carried out at 333 K under reflux and vigorous stirring. At various reaction times products were collected and analyzed through a capillary gas chromatograph (Shimadzu R 14A, equipped with FID). Products are identified through gas chromatographic injection of authentic samples and GC MS (splitting pattern) analysis. Concentration of residual H_2O_2 after each run was measured electrochemically. H_2O_2 selectivity was calculated as the amount of H_2O_2 consumed in the formation of oxidized products.

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0021-9517/98 $25.00

TABLE 1

Dihydroxylation of Unsaturated Alcohols over TS-1/H_2O_2 System[a]

Entry	Substrate	Time (h)	Conv. (%)	H_2O_2 Sel. (%)	Product selectivities (%)				
					Triol	Epoxide	Aldehyde	Acid	Others
1	$CH_2{=}CHCH_2OH$	4	95.0	95.0	—	96.0	4.0	—	—
2	$CH_3CH{=}CHCH_2OH$	4	95.2	95.5	95.5	0.4	4.0	0.1	—
3	$CH_3CH{=}CHCH_2OH$[b]	4	80.0	80.6	—	88.5	10.8	0.7	—
4	$CH_2{=}CHCH_2CH_2OH$	6	82.6	85.0	80.5	8.5	8.0	3.0	—
5	$(CH_3)_2C{=}CHCH_2OH$	4	89.2	80.0	63.1	—	1.6	—	35.3[c]
6	*cis*-$C_2H_5CH{=}CHCH_2OH$	6	76.8	78.7	86.6	6.6	4.4	2.4	—
7	$CH_2{=}CHCH_2CHOHCH_3$	4	90.0	96.2	81.3	—	2.1	1.0	15.6[d]
8	*cis*-$C_3H_7CH{=}CHCH_2OH$	6	70.3	73.3	86.2	3.7	5.9	4.2	—

[a] Reaction condition: 0.02 mole substrate, 0.02 mole H_2O_2 (30 wt% aqueous), catalyst (TS-1, Si/Ti = 27) 20 wt% with respect to the substrate, H_2O 10 g as dispersion medium, temperature 333 K.

[b] Using acetone (10 g) as solvent.

[c] $(CH_3)_2CHCOCH_2OH$ as shown in Scheme 1.

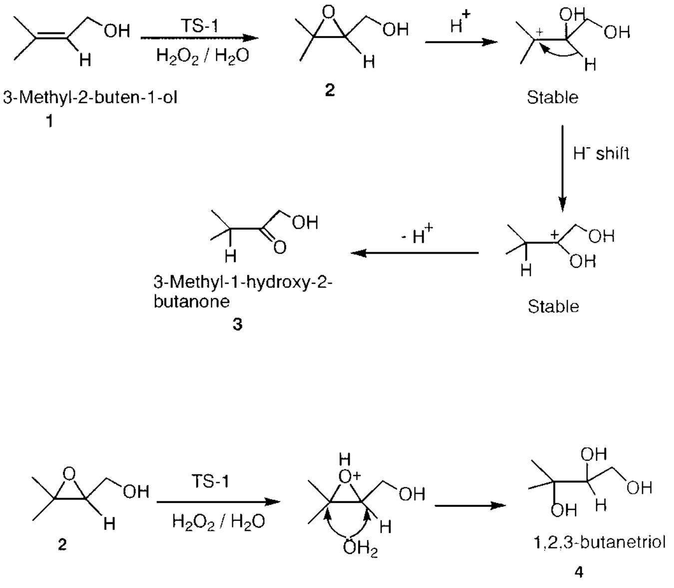
[d] 2-Methyl-4-hydroxytetrahydrofuran.

RESULTS AND DISCUSSION

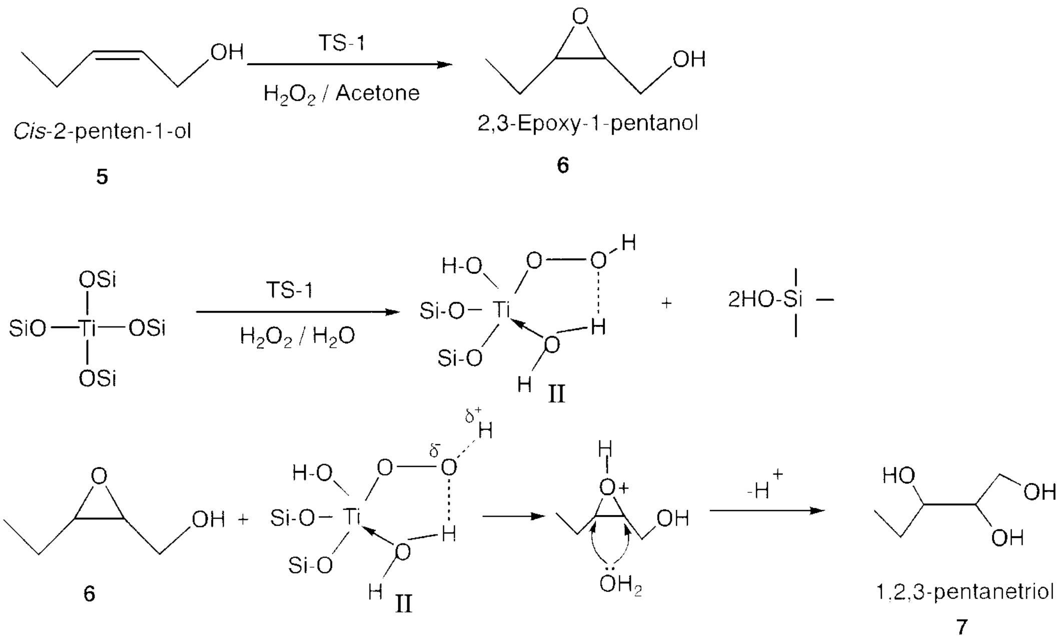
Unsaturated Alcohols

In Table 1, dihydroxylation of various unsaturated alcohols over TS-1/H_2O_2 system is presented. In the case of allyl alcohol (freely soluble in water) dihydroxylation of olefinic double bond is not observed (entry 1). However, increasing the carbon chain length from allyl to crotyl alcohol leads to a very high selectivity of the corresponding triol (1,2,4-butanetriol). In the case of crotyl alcohol, epoxide formed in the initial stages (30–60 min reaction time) of the reaction is converted to 1,2,4-butanetriol in a very fast rate. Oxidation of the alcohol functionality (i.e., CH_2OH group) occurs to a negligible extent (Table 1). In the presence of organic cosolvent acetone (biphase), however, the epoxide does not undergo hydrolysis under the identical reaction conditions (entry 3, in case of crotyl alcohol shown as a representative). Changing the position of the double bond from allylic to terminal position causes little change in the yield of the dihydroxylated product as shown in Table 1 for 3-butene-1-ol. It is noteworthy that Hutchings *et al.* (13, 14) have observed the solvolysis of glycidol to 3-ethoxy-propane-1,2-diol and 2-ethoxypropane-1,3-diol as the major products in the epoxidation of allyl alcohol over TS-1/H_2O_2 system using ethanol as solvent at 338 K.

Among the C_5 olefinic alcohols, 3-methyl-2-butene-1-ol, **1**, shows quite unusual behavior under the present triphase reaction condition. The reaction pathway is exemplified in Scheme 1. 3-Methyl-2,3-epoxy-1-butanol, **2**, formed initially would undergo intramolecular rearrangement via 1,2-shift of hydrogen to give α-hydroxyketone 1-hydroxy-3-methyl-2-butanone, **3**, to a considerable extent. Such type of hydride migration can occur in the aromatic system as observed in the epoxidation of styrene (15), where intramolecular 1,2-transfer of hydrogen in the unstable epoxide leads to the formation of phenyl acetaldehyde. 3-Methyl-2,3-epoxy-1-butanol, **2** formed in the initial stage via epoxidation of **1** can undergo two competitive reaction for the opening of oxirane ring, 1,2-hydride shift and hydrolysis. In the present case epoxy ring opening via the hydride shift competes with acid catalyzed ring opening via hydrolysis. Latter predominates and 3-methyl-1,2,3-butanetriol, **4**, is the major product (Table 1). The conversion of **1** to **3** seems to be due to the stability of tertiary carbonium ion which can be formed by the protonation of intermediate epoxide **2**. Hydride migration of this carbonium ion forms also stable tertiary carbonium ion, from which **3** forms via



SCHEME 1



SCHEME 2

deprotonation. The other epoxides cannot give stabilized tertiary carbonium ions upon protonation, producing diols as a usual consequence of oxirane hydrolysis. A similar type of migration (methyl group) in 2,3-dimethyl-2,3-epoxybutane leads to pinacolone in the presence of solid acid catalyst (16).

In the case of *cis*-2-pentene-1-ol, **5**, this type of 1,2-migration does not take place and the corresponding dihydroxylation product, 1,2,3-pentanetriol, **7** was observed as the predominant product (Scheme 2). 2,3-Epoxy-1-pentanol, **6** formed in the biphase system as the predominant product in 90.0% selectivity for acetone cosolvent. However, the titanium hydroperoxo species II in Scheme 2 generated in TS-1/H_2O_2/H_2O system under triphase has a labile Broensted proton, which activates the oxirane oxygen toward hydrolysis, leading to **7** as the major product (86.6% selectivity); it is inconceivable that the Al impurities act as the acid center in our TS-1 samples (see below). Increasing bulkiness at the active olefinic group from *cis*-2-pentene-1-ol to *cis*-2-hexene-1-ol decreases the conversion, as expected from the restricted pore openings of the MFI structure; however, selectivity for the triol remains high. Changing the position of the hydroxyl group from the primary to the secondary carbon atom causes little change in the yield of triol product. However, a small amount of by-product 2-methyl-4-hydroxytetrahydrofuran is formed due to intramolecular cyclization (Entry 7, Table 1).

Unsaturated Halides

Table 2 illustrates the conversion and diol selectivities of various allylic halides under the triphase reaction condition. Epoxides are known to be the sole product of the oxidation of allylic halides over TS-1/H_2O_2 system in the presence of cosolvents (17, 18). Allyl chloride, methallyl chloride, and crotyl chloride all show very high conversion, as well as high selectivity toward dihydroxylation. Crotyl alcohol

TABLE 2

Dihydroxylation of Unsaturated Halides over TS-1/H_2O_2 System[a]

Entry	Substrate	Conv. (mole %)	Reaction time (h)	TON (h^{-1})[b]	Product selectivities (%)		
					Diol	Epoxide	Others[c]
1	$CH_2{=}CHCH_2Cl$	98.5	6	18.6	92.3	5.2	2.5
2	$CH_2{=}CCH_3CH_2Cl$	96.6	6	15.3	90.0	6.0	4.0
3	$CH_3CH{=}CHCH_2Cl$	99.5	4	23.6	96.1	—	3.9

[a] Reaction conditions are the same as given for Table 1.
[b] Moles of substrate converted per mole of Ti per h.
[c] Include unidentified high boiling polymers.

shows higher reactivity than either allyl chloride or methallyl chloride, which is ascribed to the electrophilic character of epoxidation (5, 19); the internal double bond has higher π-electron density than the terminal double bonds. The hydrolysis of initially formed epoxides appears to proceed by an S_N1 mechanism involving carbonium ion intermediates (see below). High diol selectivity in the case of crotyl chloride compared to allyl chloride is consistent with an S_N1 mechanism, since more substituted epoxide should be more susceptible to hydrolysis.

Mechanistic Pathways

The conversion of *cis*-2-pentene-1-ol is plotted against reaction time in Fig. 1. It can be seen that the reaction proceeds faster in the triphase system than in the biphase system using acetone. Figure 2 depicts the change in the product selectivity in the *cis*-2-pentene-1-ol oxidation conducted in the triphase system. Curves a and a′ correspond to the epoxide (2,3-epoxy-1-pentanol) and dihydroxylated product (1,2,3-pentanetriol), respectively, at various reaction times. It should be noted that in the biphase system the selectivity for epoxide was kept high throughout the experiment. Figure 3 illustrates the same for allyl chloride (curves b and b′ correspond to epoxide, epichlorohydrin, and 3-chloro-1,2-propanediol, respectively). From these figures it is clear that the initial epoxidation followed by its acid hydrolysis occurs selectively at the olefinic double bond in a consecutive manner. Here it is important to mention that water used in the present triphase system not only acts as the catalyst dispersion medium but also helps to drive away the products from the active reaction sites in the zeolite channels, since the diol/triol product is much more hydrophilic than the parent substrate.

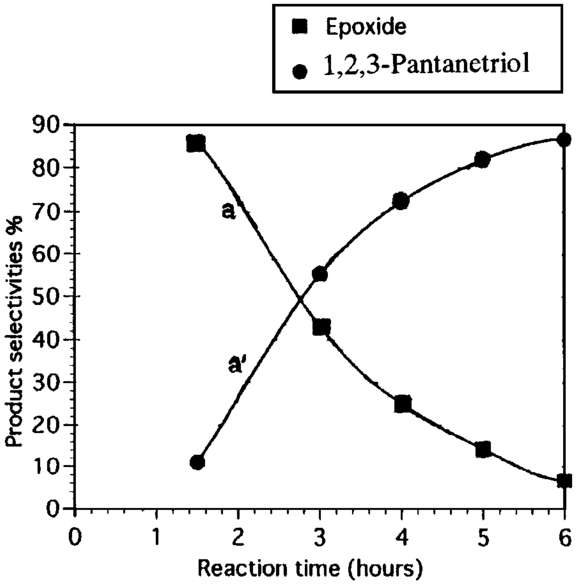


FIG. 2. Time course of product distribution in the dihydroxylation of *cis*-2-pentene-1-ol: (a) epoxide; (a′) triol.

The production of diols or their monoethers can also be obtained with modification of TS-1 by introducing trivalent elements like Al, Ga, or Fe into its MFI network (21) in the presence of a suitable solvent. These bifunctional catalysts give rise to large amounts of diols under conditions in which pure TS-1 produces only epoxides. TS-1 used in the present study is devoid of any impurity of these trivalent elements (as revealed by ICP chemical analysis of the source tetraethyl orthosilicate and tetrapropyl ammonium hydroxide and the product TS-1). Thus it is reasonable that the acidity of TS-1 in the present triphase vis-a-vis biphase (using solvent) is the inherent nature of the active site under the reaction conditions.

In Scheme 2, the mechanistic pathway for the dihydroxylation reaction (*cis*-2-pentene-1-ol is taken as a

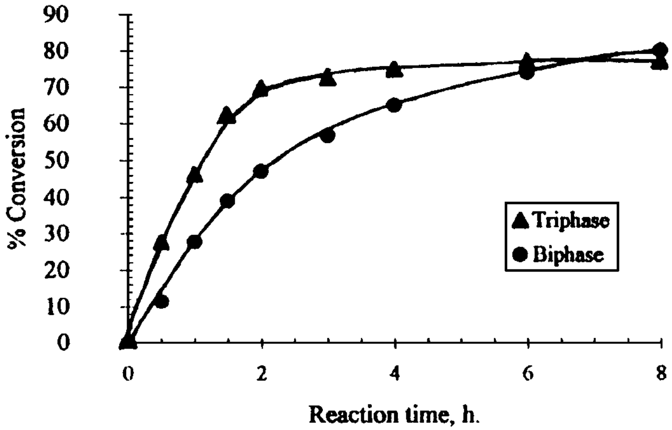


FIG. 1. Reaction kinetics of the oxidation of *cis*-2-pentene-1-ol over TS-1/H_2O_2 system under triphase (▲) and biphase (●) reaction conditions.

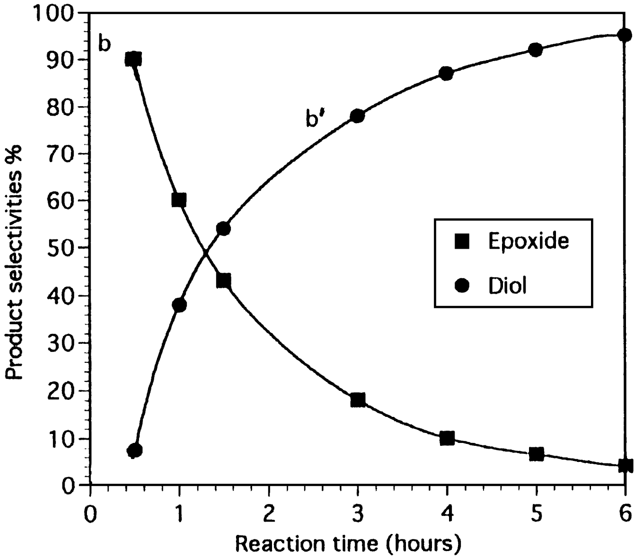


FIG. 3. Time course of product distribution in the dihydroxylation of allyl chloride: (b) epoxide; (b′) diol.

representative) is shown. The titanium hydroperoxo complex (II) (22, 23) generated in the presence of H_2O_2 and H_2O over TS-1 has a labile proton which is responsible for its acidic behavior, affecting the acid-catalyzed epoxide ring opening. High stability of this titanium hydroperoxo complex (possibly due to a five-membered ring formation through hydrogen bonding, II) under the present reaction conditions in turn leads to high H_2O_2 efficiency (80–95%, even at substrate : H_2O_2 molar ratio = 1 : 1) towards the dihydroxylation reaction.

From the above results it is clear that hydrophilic epoxides (as in the case of the epoxide of allyl alcohol, glycidol, which is freely soluble in water), being solvated by the water molecules, are in turn dragged away from the active reaction sites of the catalyst by the water molecules to be recovered as such. In contrast, relatively hydrophobic epoxides (in the case of C_4–C_6 olefinic alcohols as given in Table 1) being repelled by the water molecules surrounding the catalyst have more chance to interact with active titanium hydroperoxo sites and thus dihydroxylation is facilitated. This is further reflected in the reaction profile for the oxidation as shown in Figs. 2 and 3, which show the initially formed epoxides are converted to diols in a consecutive fashion. The epoxide of allyl chloride, epichlorohydrin is only slightly soluble (6.6 wt% at 293 K) in water, being susceptible to hydrolysis at a faster rate than the epoxide of *cis*-2-pentene-1-ol. In the presence of acetone (biphase), however, we observed the selectivity for the epoxides remained high, probably because the epoxides are efficiently expelled from the catalyst by the solvent to persist as such; the epoxides are obtained in high selectivity, 88.5 and 90.0%, from 2-butene-1-ol and *cis*-2-pentene-1-ol, respectively.

CONCLUSIONS

Titanium silicate molecular sieve, TS-1, in the presence of H_2O_2/H_2O under triphase condition, acts as a highly efficient and selective dihydroxylation catalyst. Bifunctional behavior (oxidation and acidic) of TS-1 under present reaction conditions promotes the conventional two-step dihydroxylation (the formation of epoxide followed by its hydrolysis) as a rapid one pot process. High stability of titanium hydroperoxo species in the present reaction conditions, and high hydrophilicity of the product (diol and triols) compared to the substrate and epoxy intermediate facilitate the catalytic reaction in the presence of water as a dispersion medium.

ACKNOWLEDGMENT

A.B. thanks the Japan Society for the Promotion of Science for financial assistance.

REFERENCES

1. Nieuwenhze, V., and Sharpless, K. B., *J. Am. Chem. Soc.* **115**, 7846 (1993).
2. Corey, E. J., Noe, M. C., and Guzman-Perer, A., *J. Am. Chem. Soc.* **117**, 10817 (1995).
3. Notari, B., *Stud. Surf. Sci. Catal.* **37**, 413 (1987).
4. Sheldon, R. A., *Stud. Surf. Sci. Catal.* **66**, 573 (1991).
5. Tatsumi, T., Yako, M., Nakamura, M., Yuhara, Y., and Tominaga, H., *J. Mol. Catal.* **78**, L 41 (1993).
6. Schroder, M., *Chem. Rev.* **80**, 187 (1980).
7. Wolfe, S., Ingold, C. F., and Lemieux, R. U., *J. Am. Chem. Soc.* **103**, 938 (1981).
8. Sharpless, K. B., Teranishi, A. V., and Backval, J.-E., *J. Am. Chem. Soc.* **99**, 3120 (1977).
9. Rickborn, R., and Murphy, D. K., *J. Org. Chem.* **34**, 3209 (1969).
10. Parker, R. E., and Isaacs, N. S., *Chem. Rev.* **59**, 737 (1959).
11. Weissberger, A. (Ed.), "The Chemistry of Heterocyclic Compounds," Vol. 19, Part 1, p. 270. Wiley, New York, 1964.
12. Lamaty, G., Maloq, R., Selve, C., Sivade, A., and Wylde, J., *J. Chem. Soc. Perkin Trans.* **2**, 1119 (1975).
13. Bhaumik, A., and Kumar, R., *J. Chem. Soc. Chem. Commun.*, 349 (1995).
14. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., *J. Catal.* **131**, 1 (1991).
15. Hutchings, G. J., and Lee, D. F., *J. Chem. Soc. Chem. Commun.*, 1095 (1994).
16. Hutchings, G. J., and Lee, D. F., *Catal. Lett.* **33**, 369 (1995).
17. Kumar, S. B., Mirajkar, S. P., Pais, G. C. G., Kumar, P., and Kumar, R., *J. Catal.* **156**, 163 (1995).
18. Elings, J. A., Downing, R. S., and Sheldon, R. A., *Stud. Surf. Sci. Catal. B* **105**, 1125 (1996).
19. Clerici, M. G., and Ingallina, P., *J. Catal.* **140**, 71 (1993).
20. Alvaro, M., Corma, A., Garica, H., and Valencia, S., *Appl. Catal. A: General* **128**, L7 (1995).
21. Bellussi, G., Carati, A., Clerici, M. G., and Esposito, A., *Stud. Surf. Sci. Catal.* **63**, 421 (1991).
22. Bellussi, G., Carati, A., Clerici, M. G., Maddinelli, G., and Millini, R., *J. Catal.* **133**, 220 (1992).
23. Bhaumik, A., Kumar, P., and Kumar, R., *Catal. Lett.* **40**, 47 (1996).