Angewandte Chemie

Heterogeneous Catalysis

In Situ Magnetic Resonance Investigation of Styrene Oxidation over TS-1 Zeolites**

Jianqin Zhuang, Gang Yang, Ding Ma, Xijie Lan, Xiumei Liu, Xiuwen Han, Xinhe Bao,* and Ulrich Mueller*

As an efficient catalyst for the selective oxidation of various organic substrates,[1] the titanium molecular sieve TS-1 has shown great potential in industry, as it is also environmentally benign. Over the past few decades, the synthesis of TS-1 as well as novel reactions based on it, including the mechanisms of these reactions, have attracted the attention of many researchers from experimental and computational fields.[1–6]

For example, with aqueous H_2O_2 as the oxidant, alkenes are converted into epoxides with high efficiency under mild conditions. With FTIR spectroscopy, Frei and Lin observed the TiOOH species that was determined to be the active site in the oxidation of small olefins.[6] When the reaction was extended to styrene, however, the main product was phenylacetaldehyde (PADH), and only a small amount of epoxide was obtained.[1c,3] Accompanying by-products included benzaldehyde (BADH) from cleavage of the C–C bond and 1-phenyl-1,2-ethanediol (DIOL) from hydrolysis in the presence of water.[3b] Some reports claimed that a synergic effect of TiOOH and a polar solvent (such as water) provided an acidic environment and thus promoted the isomerization or hydrolysis of styrene epoxide.[3,4] However, contrary opinions have been voiced based on the fact that the rearrangement of styrene epoxide is difficult owing to its high stability under the reaction conditions.[5] The oxidation of styrene may instead proceed by a radical mechanism with help from the aromatic π ring. Therefore, PADH might be obtained directly from

---

[*] Dr. J. Zhuang, G. Yang, Dr. D. Ma, X. Lan, X. Liu, Prof. X. Han, Prof. Dr. X. Bao
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
Dalian 116023 (P.R. China)
E-mail: dma@dicp.ac.cn
xhbao@dicp.ac.cn

Dr. D. Ma
School of Chemistry
University of Bristol
Bristol, BS8 1TS (UK)
Fax: (+44) 117-925-1295

Dr. J. Zhuang, Dr. U. Mueller
BASF Aktiengesellschaft
GCC/Z–M301
67056 Ludwigshafen (Germany)

[**] Financial support from the National Natural Science Foundation and the Ministry of Science and Technology of the People's Republic of China is gratefully acknowledged. The authors thank Dr. R. Hong and X. Ruan for helpful discussions and K. Perkin for his kind help in composing this paper.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200461113

styrene, with the formation of styrene epoxide being a competitive process. Kumar et al. used EPR spectroscopy to observe the formation of Ti–superoxo radicals in TS-1 catalysts upon contact with H_2O_2 or urea–hydroperoxide (UHP). The key site was determined to be a Ti–superoxo species such as TiOOH or TiOO$^\bullet$.[4a,6] However, there was no direct evidence for how PADH and styrene epoxide were formed, and the overall reaction is still far from being understood.

In the present work, in situ NMR spectroscopy, one of the most powerful tools for the study of catalytic mechanisms,[7–9] was applied to study the oxidation of styrene over TS-1 zeolites with UHP. The role of the Brønsted acidic sites, the catalytically active sites, and the intermediates of PADH formation were investigated. To supplement the NMR data, EPR spectroscopy was also used. This technique is very sensitive to paramagnetic species with one or more unpaired electrons, and enables the detection of even small amounts of the active sites or reaction intermediates. Through the combination of density functional theory with the gauge-invariant atomic orbital (GIAO) method, the ^{13}C chemical shifts of some key products were calculated. Then, a mechanism for the overall reaction was proposed and verified by subsequent density functional calculations.

Two kinds of TS-1 zeolite samples were used in the study: one without Brønsted acidity (sample **A**) and one with Brønsted acidity (sample **B**). The acidity was confirmed by ^{31}P MAS NMR spectroscopy with trimethylphosphane (TMP) as the probe (see the Supporting Information). When β-^{13}C-enriched styrene was adsorbed on sample **A**, two peaks centered at $\delta = 113.2$ and 128.0–140.0 ppm were observed (Figure 1 A). These peaks correspond to the β carbon atom and the other carbon atoms in styrene, respectively. When styrene was adsorbed on premixed UHP and sample **A**, the conversion of styrene can be observed (Figure 1 B). In addition to the signals of the reactant, two narrow peaks centered at $\delta = 50.2$ and 102.2 ppm appeared. The former is a typical signal for the β carbon atom of styrene epoxide, which is formed by the epoxidation of styrene with UHP.[4a,10] The latter signal is in the range for O-C-O species and assigned to a hemiacetal species **1** bound to framework Ti species of the zeolite. The local structure of the hemiacetal species was optimized by density functional calculations, and then the ^{13}C chemical shift was computed by the GIAO method (see the Supporting Information). The calculated chemical shift of this species is $\delta = 102.7$ ppm, in agreement with the experimental value of $\delta = 102.2$ ppm. In addition, a broad peak at $\delta = 64.0$–68.0 ppm appeared, which can be assigned to a glycol species bound to the framework Ti species. This assumption was confirmed by calculation of the chemical shift at $\delta = 64.7$ ppm for the corresponding structure **2** (see the Supporting Information).

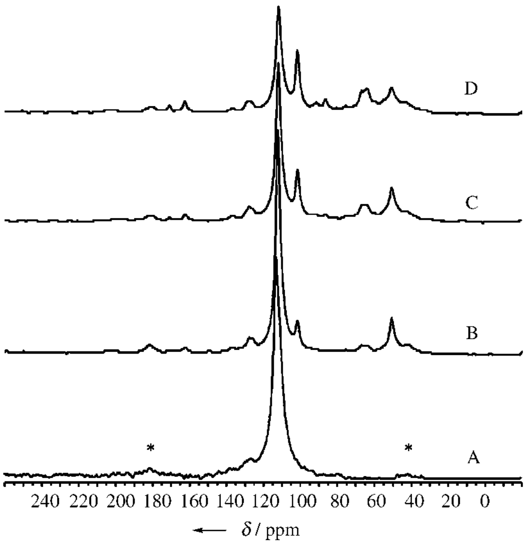
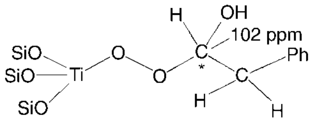
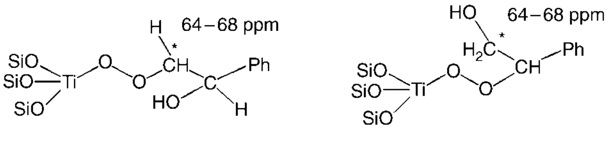


Figure 1. The in situ ^{13}C MAS NMR spectra of styrene adsorbed on sample **A** (A), and for the reaction of styrene with a mixture of sample **A** and UHP at 313 K after 0 min (B), 15 min (C), and 45 min (D). The asterisks represent side bands.



1



2

When the sample was heated at 313 K after adsorption, the intensity of the signal for the hemiacetal species increased at the expense of that of styrene (Figure 1 C, D). Meanwhile, the intensity of the signal for the styrene epoxide decreased slightly and, at the same time, a broad peak at $\delta = 64.0$–68.0 ppm appeared. In addition there were two other new peaks: one centered at $\delta = 163.2$ ppm is ascribed to formic acid, arising from further oxidation of styrene, and one at $\delta = 87.0$ ppm is due to an alkoxy group, whose nature needs further investigation. It is important that no signal at $\delta = 200$ ppm corresponding to PADH, the dominant product for styrene oxidation with aqueous H_2O_2, was detected.

Based on these results, it is clear that, with UHP as the oxidant, styrene was mainly converted into the hemiacetal species when catalyzed by TS-1 zeolite without Brønsted acid sites. On the other hand, the concentration of the side product, styrene epoxide, decreases slightly with increasing reaction time (Figure 1 B–D), suggesting that it may be in equilibrium with other minor products. The hemiacetal species are stabilized by the framework of the TS-1 zeolite and thus cannot be released. Therefore, without Brønsted acid sites, styrene could not be converted into PADH.

However, when TS-1 zeolite containing Brønsted acid sites (sample **B**) is used, a different picture is presented. Most importantly, after styrene reacted with a premixture of UHP and sample **B** (Figure 2 C) for 15 min at 313 K, a new peak at around $\delta = 202.0$ ppm appeared. The intensity of the signals for the corresponding species increased as the reaction

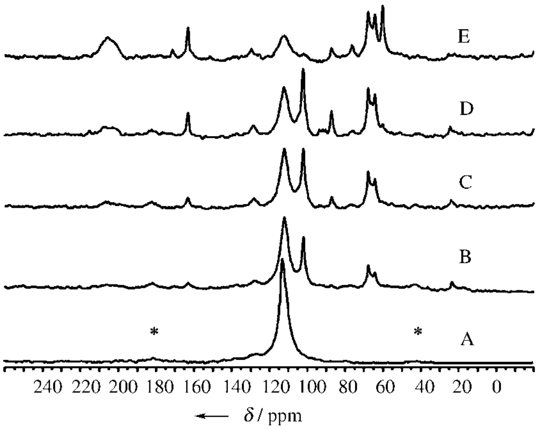


Figure 2. The in situ ^{13}C MAS NMR spectra of styrene adsorbed on sample **B** (A), and for the reaction of styrene with a mixture of sample **B** and UHP at 313 K after 0 min (B), 15 min (C), and 45 min (D). The asterisks represent side bands.

proceeded (Figure 2D, E). On the other hand, the intensity of the signal for the hemiacetal species ($\delta = 102.2$ ppm) increased at first and passed through a maximum at the same time as the depletion of styrene and the formation of PADH, strongly suggesting that the hemiactetal species are intermediates for PADH production. This rules out the previous assumption that PADH results from the rearrangement of styrene epoxide.[4] The intermediate role of the hemiacetal species in the production of PADH is in agreement with the well-documented equilibrium between hemiacetal and acetal, that is, the hemiacetal can be converted into the acetal under acidic conditions.[11] Significantly, the only difference between the two samples is that sample **B** contains Brønsted acid sites; that is, Brønsted acid sites catalyzed the conversion of hemicactal into PADH. Without Brønsted acid sites, PADH is not formed, and the hemiacetal species remains bound to the zeolite framework (Figure 1).

Much to our surprise, if a mixture of sample **A** and UHP is put aside overnight at room temperature and then allowed to react with styrene, no hemiacetal species is formed (Figure 3).

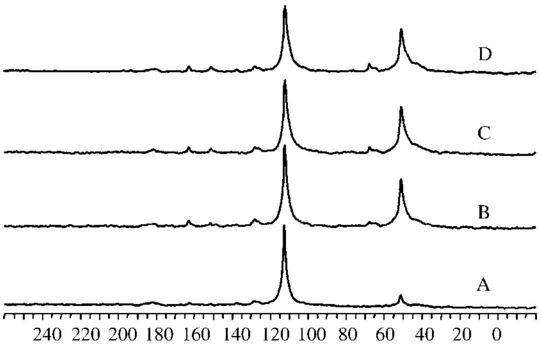


Figure 3. The ^{13}C MAS NMR spectra of styrene upon reaction with a mixture of UHP and sample **A** at 313 K after 0 min (A), 10 min (B), 20 min (C), and 40 min (D). Before the adsorption of styrene, the mixture of UHP and sample **A** was stored at room temperature overnight.

The sole product was a small amount of styrene epoxide ($\delta = 50.2$ ppm). As the reaction proceeded, trace amounts of two other minor products were observed, such as a glycol species at about $\delta = 68.0$ ppm; no aldehyde was detected. This result was completely different from that obtained upon the immediate adsorption of styrene onto the mixture of sample **A** and UHP (Figure 1), implying that the catalytic species responsible for the formation of the hemiacetal had decomposed during the long delay. This interesting phenomenon prompted us to investigate in detail the effect of delay time on the product distribution. Figure 4 depicts the ratio of the hemiacetal species to epoxide as a function of delay time. The ratio decreased as the delay time increased, and after a 12-h delay, the hemiacetal species was no longer present (Figure 3).

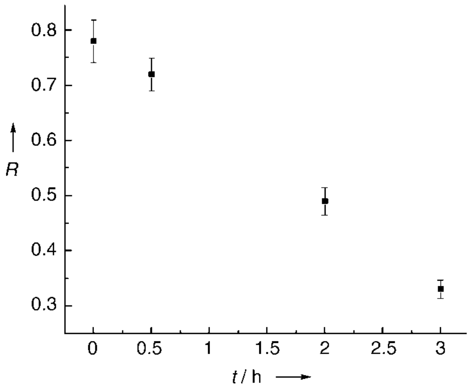


Figure 4. Plot showing the ratio *R* of hemiacetals to epoxide as a function of delay time before styrene adsorption/reaction. This ratio decreased with an increase in delay time. The intensities of the different species were obtained by integrating the area under corresponding peaks in the ^{13}C MAS NMR spectra.

We also followed the styrene oxidation by in situ EPR spectroscopy. Figure 5a shows the EPR spectra of sample **A** and UHP at room temperature with different delay times. Two distinct signals were observed, which indicated the existence of different Ti^{4+} sites in the mixture. The stronger signal ($g_x = 2.0023$, $g_y = 2.0090$, $g_z = 2.0280$) was assigned to the Ti–superoxo species from the interaction between the framework Ti and UHP. The other weak resonance at $g_z = 2.0200$ was caused by the $(SiO)_2(OH)TiOO^{-\bullet}$ species, that is, the defects in the TS-1 zeolite[12] or the superoxo anion dispersed on extra framework Ti sites.[13] As time went on, the signal at $g_z = 2.0280$ gradually wore off, whereas the signal at $g_z = 2.0200$ remained almost unchanged, indicating that the Ti–superoxo species in the framework Ti sites was not stable and easily quenched. When this result is coupled with that from the NMR experiment, in which the ratio of hemiacetal to epoxide decreased with the delay time, it is clear that production of the hemiacetal species decreased with quenching of the Ti–superoxo species. Thus it is natural to conclude that the Ti–superoxo species was critical in the formation of the hemiacetal species, that is, it represents the active center for the formation of the hemiacetal species. To further support this conclusion, different amounts of styrene were

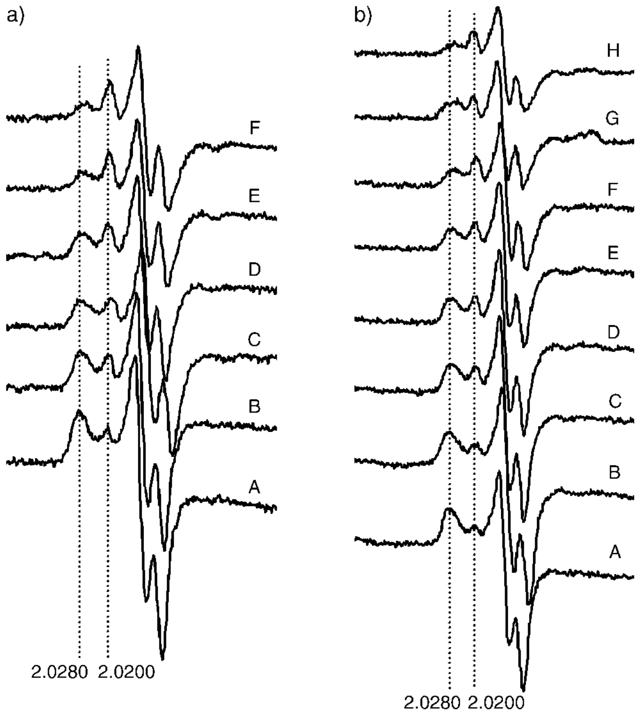
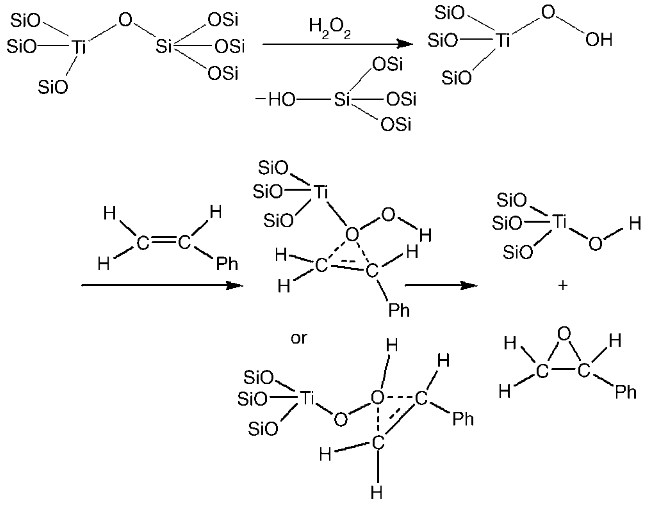


Figure 5. a) The EPR spectra of sample **A** after interaction with UHP at RT for different lengths of time: A) 0 min, B) 20 min, C) 30 min, D) 45 min, E) 55 min, F) 90 min. b) The EPR spectra of the reaction of sample **A** and UHP with different amounts of styrene: A) 0 mL, B) 0.05 mL, C) 0.10 mL, D) 0.15 mL, E) 0.20 mL, F) 0.25 mL, G) 0.50 mL, H) 0.75 mL.

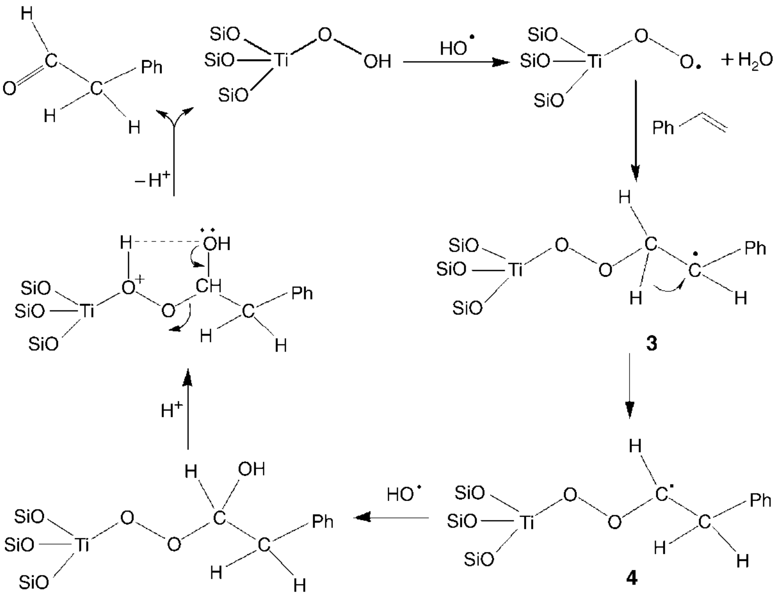


Scheme 1. The proposed mechanism for the formation of TiOOH and styrene epoxide.

added to the mixture of TS-1 and UHP at 293 K (without delay time). Indeed, the signal at $g_z = 2.0280$ decreased in intensity as the Ti–superoxo species was consumed by the additional styrene, whereas the signal at $g_z = 2.0200$ remained almost intact (Figure 5b). This again proved that the Ti superoxo radical species formed on tetrapodal Ti ions was involved in the oxidation of styrene and is responsible for the formation of the hemiacetal species.

It is generally accepted that the first step in the oxidation by the TS-1/H_2O_2 system is the formation of the TiOOH species, the species responsible for the epoxidation.[1b,2d,14] While the production of the epoxide species was not disturbed by a delay in reaction, it is clear that it is formed at a different active center than the hemiacetal species, the precursor of PADH. This is different from previous studies that suggested that PADH is just the rearrangement product of epoxide.[4] As TiOOH is the precursor for the generation of the Ti–superoxo species (by the reaction $TiOOH + HO^{\bullet} \rightarrow TiOO^{\bullet} + H_2O$),[15] the epoxidation and the radical reaction to form the hemiacetal/PADH are competitive processes.

Based on these results and the theoretical calculations (see the Supporting Information), a mechanism for the oxidation of styrene is proposed (Schemes 1 and 2). First, the framework Ti species (which may be distorted[16]) reacts with H_2O_2 to form TiOOH. Second, TiOOH either oxidizes styrene to styrene epoxide or reacts with the $OH^{\bullet}$ radical (generated from the decomposition of H_2O_2) to form the Ti–superoxo radical species. Third, the superoxo species interacts with the C–C double bond of styrene to form a new organic radical **3**, which is immediately converted into another radical **4** through hydrogen transfer from the β-C atom to the α-C atom of the styrene side chain. According to the theoretical calculations this process is thermodynamically favorable (see the Supporting Information). Finally, the $OH^{\bullet}$ radical terminates the chain reactions and form the hemiacetal species (^{13}C MAS NMR signal at $\delta = 102.2$ ppm). Without Brønsted acid sites (as with sample **A**,



Scheme 2. The proposed mechanism for the radical reaction leading to the hemiacetal species and PADH.

Figure 1) the hemiacetal species is stable on the catalyst surface and with Brønsted acid sites (sample **B**) it is converted into aldehyde and then released from the zeolite framework (Figure 2). At the same time, TiOOH is recovered and thus the catalytic cycle is accomplished.

In summary, the mechanism of styrene oxidation by TS-1/UHP is discussed in detail. It was verified that the Ti–superoxo radical is responsible for the formation of the hemiacetal species, while Brønsted acid sites offer the active centers for the transformation of the hemiacetal species to PADH. Without these Brønsted sites, the hemiacetal species remain stable on the framework of TS-1, and accordingly no PADH is formed. Therefore, styrene epoxide and PADH are formed by two competing processes: PADH does not result from further reaction of styrene epoxide, as previously suggested. Through the combination of experimental results and theoretical calculations, a more reasonable mechanism for styrene oxidation has been proposed.

Experimental Section

The two different TS-1 zeolites with (sample **B**) or without (sample **A**) Brønsted sites were synthesized according to a BASF Aktiengesellschaft patent (WO 01/14251). X-ray diffraction confirmed the MFI structure of both samples. Chemical analysis was performed with a SRS 3400 X-ray fluorescence spectrometer. The overall SiO_2/TiO_2 ratios of these samples are 50 (sample **A**) and 52 (sample **B**).

The acidity in the samples was characterized by ^{31}P MAS NMR spectroscopy of trimethylphosphane (TMP) adsorbed on TS-1 zeolites. The samples were dehydrated by heating at 673 K under vacuum (below 10^{-2} Pa) for 20 h. The adsorption of TMP (Acros Organics) was performed by exposing the dehydrated sample to a saturated vapor pressure at room temperature for 30 min. Each sample was then evacuated for 20 min to remove the TMP physisorbed on the surface. The sample was then filled into an NMR rotor and sealed without exposure to air.

In situ ^{13}C MAS NMR spectra were measured by adsorbing β-^{13}C-rich styrene (Cambridge Co.) on samples **A** and **B** with a homemade device. Before adsorption the samples were dehydrated by heating at 673 K under vacuum (below 10^{-2} Pa) for 20 h and then used directly or mixed with urea–hydroperoxide (Acros Organics) uniformly under N_2. The mixture was evacuated at room temperature for 5 min and styrene was then loaded at −196 °C (liquid nitrogen). The sample was evacuated for 20 min to remove physisorbed styrene. Subsequently, it was treated at 313 K for a precisely controlled period of time, and then packed into the rotor.

All NMR spectra were obtained at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4-mm ZrO_2 rotors. The ^{31}P MAS NMR spectra with high-power proton decoupling were obtained at 161.9 MHz by using a 2.0-μs pulse, 2-s repetition time, and 1024–2048 scans; the samples were spun at 6 kHz and referenced to 85 % H_3PO_4. The ^{13}C MAS NMR measurements were made at 100.6 MHz with high-power proton decoupling by using a 2-μs pulse and 2-s repetition time. For each ^{13}C spectrum, 1600 free induction decays were accumulated with a sample spinning rate of 7 kHz. Adamantane was used as the reference of the chemical shift. The WINNMR program supplied by the instrument manufacturer was employed for spectral deconvolution by using Gaussian–Lorentzian lineshapes.

EPR spectra were recorded on a JEOL ES-EDX3 spectrometer. Prior to the measurements, the samples (100 mg) were dehydrated at 673 K for 2 h under He and then mixed with 30 mg of UHP. The EPR spectra were recorded at room temperature, operating at an X-band frequency of 9.42 GHz and 100 kHz field modulation with a microwave power of 1 mW. The g factors were calculated by taking the signal of manganese as standard.

Received: June 29, 2004

Keywords: EPR spectroscopy · heterogeneous catalysis · NMR spectroscopy · styrene oxidation · zeolites

---

[1] a) D. R. C. Huybrechts, L. De Braycker, P. A. Jacobs, *Nature* **1990**, *345*, 240; b) M. G. Clerici, P. Ingallina, *J. Catal.* **1993**, *140*, 71; c) J. Q. Zhuang, D. Ma, Z. M. Yan, X. M. Liu, X. Han, X. Bao, Y. Zhang, X. Guo, X. Wang, *Appl. Catal. A* **2004**, *258*, 1; d) A. Thangaraj, R. Kumar, P. Ratnasamy, *J. Catal.* **1991**, *131*, 294; e) A. Thangaraj, S. Sivasanker, P. Ratnasamy, *J. Catal.* **1991**, *131*, 394.

[2] a) M. Taramasso, G. Perego, B. Notari, US Patent 4410501, **1983**; b) G. Tozzola, M. A. Mantegazza, G. Ranghino, G. Petrini, S. Bordiga, G. Ricchiardi, C. Lamberti, R. Zulian, A. Zecchina, *J. Catal.* **1998**, *179*, 64; c) G. N. Vayssilov, *Catal. Rev.* **1997**, *39*, 209; d) S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti, A. Zecchina, *Angew. Chem.* **2002**, *114*, 4928; *Angew. Chem. Int. Ed.* **2002**, *41*, 4734; e) P. E. Sinclair, C. R. A. Catlow, *J. Phys. Chem. B* **1999**, *103*, 1084; f) P. F. Henry, M. T. Weller, C. C. Wilson, *J. Phys. Chem. B* **2001**, *105*, 7452.

[3] a) S. B. Kumar, S. P. Mirajkar, G. C. G. Pais, P. Kumar, *J. Catal.* **1995**, *156*, 163; b) M. A. Uguina, D. P. Serrano, R. Sanz, J. L. G. Fierro, M. Lopez Granados, R. Mariscal, *Catal. Today* **2000**, *61*, 263.

[4] a) S. L. Laha, R. Kumar, *J. Catal.* **2001**, *204*, 64; b) G. Bellussi, A. Carati, M. G. Clerici, G. Maddinelli, R. Millini, *J. Catal.* **1992**, *133*, 220.

[5] G. R. Wang, B. Wang, X. F. Zhang, Y. Z. Wang, H. O. Liu, X. W. Guo, X. S. Wang, *J. Dalian Univ. Technol.* **2000**, *40*, 160.

[6] W. Y. Lin, H. Frei, *J. Am. Chem. Soc.* **2002**, *124*, 9292.

[7] M. Hunger, J. Weitkamp, *Angew. Chem.* **2001**, *113*, 3040; *Angew. Chem. Int. Ed.* **2001**, *40*, 2954.

[8] a) C. A. Fyfe, Y. Feng, H. Grondey, G. T. Kokotailo, H. Gies, *Chem. Rev.* **1991**, *91*, 1525; b) I. I. Ivanova, E. G. Derouane, *Stud. Surf. Sci. Catal.* **1994**, *85*, 357.

[9] a) E. Karlsen, K. Schoffel, *Catal. Today* **1996**, *32*, 107; b) M. Neurock, L. E. Manzer, *Chem. Commun.* **1996**, 1133.

[10] a) D. Srinivas, P. Manikandan, S. C. Laha, R. Kumar, P. Ratnasamy, *J. Catal.* **2003**, *217*, 160; b) S. C. Laha, R. Kumar, *J. Catal.* **2002**, *208*, 339.

[11] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill, New York, **1977**, p. 804.

[12] G. Sanker, J. M. Thomas, C. R. A. Catlow, C. M. Barker, D. Gleeson, N. Kaltsoyannis, *J. Phys. Chem. B* **2001**, *105*, 9028.

[13] Q. Zhao, X. H. Bao, Y. Wang, L. W. Lin, G. Li, X. W. Guo, X. S. Wang, *J. Mol. Catal. A* **2000**, *157*, 265.

[14] B. Notari, *Adv. Catal.* **1996**, *41*, 253.

[15] F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti, G. Petrini, *Catal. Lett.* **1992**, *16*, 109.

[16] J. Q. Zhuang, D. Ma, Z. M. Yan, F. Deng, X. M. Liu, X. W. Han, X. H. Bao, X. Wu Liu, X. Guo, X. Wang, *J. Catal.* **2004**, *221*, 670.