NaY Zeolite as Host for the Selective Heterogeneous Oxidation of Silanes and Olefins with Hydrogen Peroxide Catalyzed by Methyltrioxorhenium

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The methyltrioxorhenium(MTO)-catalyzed oxidation of silanes to silanols and the epoxidation of various olefins by aqueous 85% H_2O_2 proceed in high yields and excellent product selectivities (no disiloxanes, diols) in the presence of the zeolite NaY. The oxidative species is located inside the 12-Å supercages. This prevents the bimolecular condensation of the silanol to disiloxane by steric means and the Lewis-acid assisted hydrolysis of the epoxide to the diol.

Introduction

Methyltrioxorhenium (MTO), the so-called Herrmann catalyst,[1] has been the subject of intensive investigations since its discovery.[2] This versatile and highly active rhenium complex catalyzes numerous oxyfunctionalizations such as epoxidation,[3] heteroatom oxidation,[4] and C−H[5] as well as Si−H oxidations[6] by activating the cheap and environmentally benign but reluctant oxidant H_2O_2. Despite these advantages, the drawbacks of the MTO/H_2O_2 oxidation system are low conversions and appreciable formation of side products, due to the facile decomposition of MTO to the perrhenate.[8] For example, in epoxidations the epoxide ring is opened quite readily to the diol,[7] which suffers pinacol-type rearrangement and cleavage.[3a] In silane oxidations, the undesirable disiloxane is frequently formed as the major product[6] through acid-catalyzed condensation. Pyridine[9] and pyrazole[10] as Lewis acid buffers overcome these drawbacks by coordination to the metal center, thereby reducing the Lewis acidity of the catalyst and promote stability against decomposition to the perrhenate. Consequently, such additives greatly enhance the efficiency and selectivity of MTO-catalyzed oxidations.[11]

As an alternative approach to circumvent such detrimental side reactions by the MTO/H_2O_2 oxidant, we have recently shown the efficacy of the hydrogen peroxide adduct (UHP) as oxygen source in oxyfunctionalizations catalyzed by MTO.[3a,6] Thus, the heterogeneous MTO/UHP oxidant (UHP is not soluble in the organic reaction medium, e.g., CH_2Cl_2) also exhibits high conversions and selectivities in olefin epoxidations and silane oxidations.[3a,6] Instead of the buffering action of the MTO/pyridine[9] combination, host−guest chemistry was proposed for the MTO/UHP system, for which the oxidation takes place inside the urea channels and formation of the disiloxane side product is prevented due to spatial constraints.[6,12] To place this (for urea) novel concept on a rigorous experimental basis, it was decided to employ a zeolite as host for MTO/H_2O_2 oxidations. Herein we report our results on NaY as a heterogeneous host for MTO-catalyzed epoxidations and silane oxidations; this zeolite is widely used for shape-selective oxidations with other organometallic compounds.[13] The similarity of the NaY/MTO/H_2O_2 and the MTO/UHP oxidants, i.e., high efficiency and selectivity, establishes host−guest chemistry in these heterogeneous oxyfunctionalizations.

Results and Discussion

Silane Oxidations. The MTO-catalyzed reactions were carried out at ambient temperature (ca. 20 °C) in methylene chloride in the presence of unactivated zeolite. In contrast to the previously reported preparation of NaY/MTO by vacuum sublimation in the presence of a highly activated zeolite under strictly anhydrous conditions,[14] we found that mixing the unactivated zeolite with H_2O_2, the substrate, and MTO was beneficial for the conversion and product distribution in the silane oxidations. Activa-

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Table 1. Mass Balances, Conversions, and Product Selectivities for the MTO-Catalyzed Oxidation of Silanes by Aqueous H_2O_2 in the Presence of NaY Zeolite[a]

$$\underset{\mathbf{1}}{R_3Si\text{–}H} \xrightarrow[20\ °C,\ 24\ h]{MTO,\ [Ox.]} \underset{\mathbf{2}}{R_3Si\text{–}OH} + \underset{\mathbf{3}}{[R_3Si]_2O}$$

entry	substrate	[Ox.]	solvent	m.b.[b] (%)	convn[b] (%)	selectivity[c] **2**:**3**
1	$EtMe_2SiH$ (**1a**)	NaY/85% H_2O_2	CH_2Cl_2	>95	72	>99:1
2	$EtMe_2SiH$ (**1a**)	UHP[d]	CH_2Cl_2	77	>95	94:6
3	*t*$BuMe_2SiH$ (**1b**)	NaY/85% H_2O_2	CH_2Cl_2	85	>99	>99:1
4	*c*$HexMe_2SiH$ (**1c**)	NaY/85% H_2O_2	CH_2Cl_2	80	>99	>99:1
5	$PhMe_2SiH$ (**1d**)	NaY/85% H_2O_2	CH_2Cl_2	>95	>99	>99:1
6	$PhMe_2SiH$ (**1d**)	UHP[d]	CH_2Cl_2	>99	87	98:2
7	$PhMe_2SiH$ (**1d**)	85% H_2O_2[d]	CH_2Cl_2	>99	26	20:80
8	$PhMe_2SiH$ (**1d**)	SiO_2/85% H_2O_2[d]	CH_2Cl_2	82	28	17:83
9	$PhMe_2SiH$ (**1d**)	NaY/30% H_2O_2	CH_2Cl_2	91	17	99:1
10	$PhMe_2SiH$ (**1d**)	NaY/85% H_2O_2	MeOH	77	31	94:6
11	Et_3SiH (**1e**)	NaY/85% H_2O_2	CH_2Cl_2	74	86	99:1
12	Et_3SiH (**1e**)	UHP[d]	CH_2Cl_2	76	78	>99:1

[a] Reaction performed with 330 μmol of substrate, 2 mol % of MTO, and 2 equiv of H_2O_2 in the presence of 35 mg of NaY zeolite. [b] Entries 1 and 2: determined by ^1H NMR spectroscopy directly on the crude reaction mixture, error ±5% of the stated values. Entries 4–12: mass balances and conversions were determined by gas chromatography versus an internal standard (IS), error ±2% of the stated values. [c] Determined by gas chromatography versus an internal standard (IS), error ±2% of the stated values. [d] Data taken from ref 6.

tion of the zeolite results in low silane conversion and poor product selectivity (silanol versus disiloxane), even when pyridine was used to neutralize acidic sites in the zeolite. We ascribe this to the strong acidity of the calcinated zeolite, which presumably leads to decomposition of the MTO catalyst. As test substrate, dimethylphenylsilane (**1d**) was chosen to optimize the reaction conditions in order to achieve high silane conversions and good product selectivities (eq 1).

$$Me_2PhSi\text{-}H \xrightarrow[CH_2Cl_2,\ 20\ °C]{NaY/MTO,\ 85\%\ H_2O_2} Me_2PhSi\text{-}OH + [Me_2PhSi]_2O \tag{eq 1}$$

For this purpose, the ratios of catalyst to oxidant, catalyst to substrate, and the amount of zeolite were varied. The optimal conditions are 2 mol % of MTO, 2 equiv of H_2O_2, and 5.3 mg of zeolite per 1 μmol of MTO catalyst, which were used unless otherwise stated. No oxidation was observed without MTO. Furthermore, no decomposition of MTO to perrhenate, which efficiently catalyzes the silanol condensation,[6] was found even during prolonged reaction times and in the presence of hydrogen peroxide. The order of addition of the four reaction partners (zeolite, MTO, H_2O_2, and silane) was varied, and higher conversion and better selectivity were obtained when the zeolite and H_2O_2 were added to the silane before the MTO catalyst. The latter is very soluble in CH_2Cl_2 and has, therefore, no tendency to enter the polar interior of the zeolite. Thus, when the H_2O_2 is added last, considerable oxidation (and also catalyst decomposition) will take place in solution, which leads to low conversions and high amounts of disiloxane.[6] In contrast, when H_2O_2 is added first, it is absorbed by the zeolite and the oxidation takes place inside the zeolite, which is beneficial for high substrate (silane) conversions and product (silanol) selectivities.

To assess whether the oxidation takes place inside the zeolite, a prestirred slurry of NaY/MTO/H_2O_2 was removed by filtration and the silane **1d** added to the filtrate; no conversion was observed even after 24 h, as confirmed by GC analysis. To explore the effect of the outer zeolite surface, an experiment with SiO_2 (32–63 μm) was conducted, which mimics the outer surface of the zeolite (Table 1, entry 8).[15] Under these heterogeneous conditions, only a modest conversion to the disiloxane **3d** as the main product was found. These results establish that the oxidation takes place inside the 12 Å supercages rather than on the outer surface of the zeolite. Force-field calculations revealed that the dimensions of the silanol **2d** are 6.5 × 4.8 Å and those for the silanol-to-disiloxane condensation ca. 9.1 × 8.8 Å (core to core distances). These data suggest that two silanol molecules fit into the same supercage and that disiloxane formation inside the zeolite cavity should be feasible; however, there is a 20-fold excess of silane relative to the number of supercages and GC analysis shows that almost all of the organic material is in solution during the reaction, which makes it unlikely for two silanol molecules to meet in the same cavity. Moreover, the silanol does not dimerize spontaneously and requires activation by Lewis acids, but coordination of a rhenium species for such purpose would exceed the available space. Therefore, the high silanol selectivity (little disiloxane formation) is evidently due to the fact that two silanol molecules will not meet in the same cavity and if they did, acid-catalyzed condensation is prevented by space limitations. Further support is provided by our previous studies on the Ti-β/H_2O_2-catalyzed silane oxidation,[12] for which the same high silanol selectivities have been found. Like in the present case, space limitations of the 7.4 Å wide channel in the Ti-β zeolite prevent the silanol condensation.

To demonstrate the general scope of the catalytic NaY/MTO/H_2O_2 oxidation system, some selected silanes **1a**–**e** were oxidized (Table 1). Excellent conversions and silanol selectivities were found for NaY and CH_2Cl_2 with 85% H_2O_2 (entries 1, 3–5, and 11) as well as for the urea–H_2O_2 adduct (UHP, entries 2, 6, and 12), both heterogeneous conditions. In contrast, the homogeneous MTO-catalyzed oxidation of the silane **1d** led mainly to the disiloxane **3d** (entry 7). However, when 30% H_2O_2 was used, the conversion dropped dramatically to 17%, although the selectivity remained excellent (entry 9). Moreover, the change of the solvent from methylene chloride to methanol also resulted in a drastic drop in the conversion to 31%, but the selectivity remained as well high at 94:6 (entry 10). This trend has been previ-

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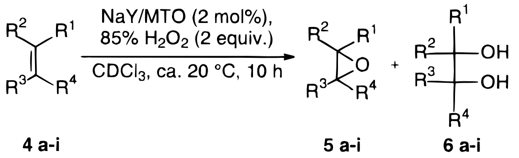
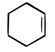
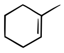
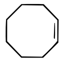
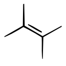
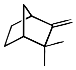
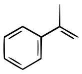
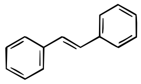
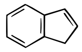
Table 2. Mass Balances, Conversions, and Selectivities for the MTO-Catalyzed Epoxidation of Alkenes by 85% H_2O_2 in the Presence of NaY Zeolite



entry	substrate	m.b.[a] [%]	convn[a] [%]	selectivity[a] 5 : 6
1	 (**4a**)	83	47	>95 : 5
2	 (**4b**)	90	42	75 : 25
3[b]		62	>95	91 : 09
4	 (**4c**)	85	33	>95 : 5
5[b]		87	95	>95 : 5
6	 (**4d**)	65	54	>95 : 5
7	 (**4e**)	79	89	>95[c] : 5
8	 (**4f**)	69	43	>95 : 5
9	 (**4g**)	80	>95	>95 : 5
10	 (**4h**)	61	52	>95 : 5

[a] Mass balance, conversion, and product ratios determined by ^1H NMR spectroscopy directly on the crude reaction mixture, error ±5% of the stated values. [b] In the presence of 12 mol % pyridine. [c] Exo/endo ratio 82:18.

ously observed and ascribed to polarity effects, since the peroxo complexes are formed faster in aprotic media.[16]

The present zeolite results are mechanistically relevant to our recent report, in which we have proposed that the efficient and selective silane oxidation by MTO/UHP takes place inside the urea channels.[6] The efficiencies and selectivities of the previous process match those for the Si−H insertion in the NaY zeolite as host of the present study (Table 1). In view of this similarity and the fact that the heterogeneous zeolite oxidation must take place in its interior, the highly efficient and selective MTO/UHP heterogeneous process evidently also involves also host−guest chemistry.

Epoxidations. A selection of olefins, which encompasses the cis- and trans-substituted **4a**,**c**,**g**,**h**, the 1,1-disubstituted **4e**,**f**, the trisubstituted **4b**, and the tetrasubstituted **4d** ones, was oxidized in the presence of the NaY zeolite under the optimized conditions developed for the oxidation of silanes (Table 2). In addition, MTO/H_2O_2/pyridine was also employed for the oxidation of the olefins **4b**,**c**, but with 85% instead of the normally used 30% H_2O_2, since for the silanes it was shown that with 30% H_2O_2 no oxidation is observed in the zeolite. The conversions were in most cases excellent; however, even after exhaustive washing with methanol, only moderate mass balances have been obtained for olefins **4b** (entry 3) with NaY/MTO/85% H_2O_2/pyridine and olefins **4d**,**h** (entries 6 and 10) with NaY/MTO/85% H_2O_2.

Little (<5%) diol was found for the NaY/MTO/85% H_2O_2 conditions, except for 1-methylcyclohexene (**4b**), whose epoxide **5b** is known to be readily hydrolyzed.[3] Even with 85% aqueous H_2O_2, the usual cleavage and rearrangement products were not observed. This may be explained by recalling some control experiments from silane oxidations. These showed that most of the organic material is in the organic phase. Furthermore, the supernatant liquid does not show any oxidation activity even in the presence of pyridine; i.e., the rhenium species is absorbed in the supercages of the zeolite. The combination of MTO/H_2O_2, however, has previously been shown to cause epoxide hydrolysis.[7] Since oxidant and epoxide are topologically separated (MTO is absorbed in the zeolite, the epoxide is in solution), formation of the diol side-product is therefore prevented.

These results represent a definite improvement in the selectivity and yields compared to MTO/H_2O_2[1] and display significantly increased epoxide selectivities compared to the previously published heterogeneous MTO system on modified silica.[17] Moreover, our data compare favorably with those obtained for MTO/UHP[3] and MTO/30%H_2O_2/pyridine,[9] albeit the conversions are lower. This drawback of the NaY/MTO/85% H_2O_2 system may be remedied by the addition of catalytic amounts of pyridine (entries 3 and 5), which also improves the selectivity. It is evident that the beneficial pyridine effect[9] in solution is also manifested in the heterogeneous epoxidation; the zeolite merely serves as microscopic reaction vessel.

Conclusion

The present results demonstrate the general applicability of the NaY zeolite as host for heterogeneous MTO reactions. For both, silane oxidation and epoxidation, high product selectivities have been obtained with aqueous 85% H_2O_2 as oxidant only in the presence of the zeolite, which acts as absorbent for the aqueous phase and prevents the MTO catalyst from decomposition.

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Supporting Information Available: Experimental procedure for the MTO-catalyzed oxidation of the silanes **1a**−**e** and olefins **4a**−**h**; GC conditions (Table 3); order of the addition of the zeolite, H_2O_2, MTO, and silane (Table 4); and the amounts of zeolite (Table 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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