

Selective oxidation of n-hexane over a titanium silicate molecular sieve with MEL structure

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(Received May 6, 1991; revised July 19, 1991)

Abstract

The selective oxidation of n-hexane to secondary alcohols and ketones has been carried out with hydrogen peroxide using TS-2, a titanium silicate molecular sieve, as the catalyst. TS-2 is found to be highly selective in the oxidation of alkanes. The influence of various parameters, such as the Ti/(Si+Ti) ratio of TS-2, its concentration, the temperature of the reaction, the feed ratio (n-C₆:H₂O₂), the nature of the solvent and the substrate (reactant) size and shape, on the activity and selectivity in the oxyfunctionalization reaction are reported.

Introduction

Titanium silicate molecular sieves are zeolite isomorphs in which Ti⁴⁺ ions are present in the lattice along with Si⁴⁺ ions [1, 2]. The pure titanium analogs do not possess the strong acidity characteristic of the aluminosilicate zeolites. However, they can catalyze interesting selective oxidation reactions in the presence of hydrogen peroxide [2–8]. The most studied titanium silicate is TS-1 [1–8], a ZSM-5 isomorph. This molecular sieve has been found to catalyze the selective oxidation of compounds such as n-alkanes [6–9] which are normally resistant to oxidation by hydrogen peroxide.

Recently the synthesis of another titanium silicate molecular sieve (called TS-2) belonging to the MEL structure group was reported [9]. Its catalytic properties are also expected to be similar to that of TS-1. However, detailed information on this aspect is not yet available in the literature. We report in this paper our studies on the catalytic activity of TS-2 in the oxyfunctionalization of n-hexane with hydrogen peroxide.

Experimental

The titanium silicate molecular sieve with MEL structure (TS-2) was synthesized by mixing tetrabutylammonium hydroxide, tetraethyl orthosilicate and titanium tetrabutoxide and autoclaving the mixture at 443 K for 48 h. The details of the synthesis and characterization of this new titanium silicate have been reported elsewhere [10, 11]. The material has been established

to be single phase (MEL-type). The as-synthesized TS-2 was filtered, washed, dried and calcined in dry air for 16 h at 823 K.

The other zeolites used in this study, *viz.* TS-1, silicalite-2, ZSM-11 and Al-TS-2, were synthesized as per published procedures [12–15] and converted into the H-form by conventional techniques.

The catalytic reactions were carried out in stirred autoclaves (Parr Instrument) of 300 ml capacity at temperatures between 323 and 398 K under autogeneous pressure, using different mole ratios of hydrogen peroxide (26 wt.% aqueous solution) and n-hexane. In order to obtain a single liquid phase, acetone was used as solvent. Typically 0.2 g of the catalyst was used (300–400 mesh). The duration of the runs was 5 h. Product analysis was carried out in a gas chromatograph (HP 5880 A) using a capillary column (HP-1, 50 m) and a FID detector.

Results and discussion

Activity of different catalysts

The oxidation of n-hexane was studied over a number of MEL isomorphs, *viz.* silicalite-2, ZSM-11, Al-TS-2 and TS-2. For comparison, a blank experiment with a high surface area amorphous silica was also carried out. An experiment was also carried out with TS-1 (MFI-type). The major products of the reaction were 2- and 3-hexanols and 2- and 3-hexanones. Small quantities of compounds with more than one functional group and lactones were also detected. However, these compounds were not analyzed in detail. Notably, 1-hexanol and hexanal were not detected.

The results are presented in Table 1. The most active catalysts are found to be TS-1 and TS-2, which are also the most selective for the formation of monofunctional compounds. Al-TS-2 containing both Al and Ti is also catalytically active. On the other samples, the activities and selectivities were very low. The smaller activity of Al-TS-2 when compared to TS-2 (both contain the same amount of Ti) is due to the rapid decomposition (and loss) of H_2O_2 by the acid (Al^{3+}) centers in the zeolite. It therefore appears that Ti^{4+} ions are responsible for the selective oxidation property of TS-2. If we examine the ratio of the 2-substituted to the 3-substituted compounds over the different catalysts (Table 1), we note that Ti activates the 2-position to a greater extent for insertion of the oxygen function. Similar results have also been reported by Huybrechts *et al.* [7] in their studies using TS-1. The larger conversion noted by us for TS-1 (compared to TS-2) could be due to differences in the structures, crystallite sizes and Ti distribution in the two samples. The average crystallite sizes of TS-2 and related (MEL) samples were between 2–3 μm while that of TS-1 was $\sim 1 \mu\text{m}$ (from SEM examination).

Influence of Ti content of TS-2

Three TS-2 samples containing different Ti contents ($\text{Ti}/(\text{Ti} + \text{Si}) = 0.033, 0.014, 0.008$) were examined for catalytic performance under identical

TABLE 1

Oxidation of n-hexane over different zeolites with MEL structure^a

Catalyst	n-C ₆ Conversion (wt.%)	H ₂ O ₂ ^b utilization (mol%)	Break-up of products (wt.%) ^c					2-/3- ratio ^d	Product ^e selectivity
			2-ol	2-one	3-ol	3-one	others		
TS-2 ^f	18.9	61.6	31.0	24.0	17.9	16.5	10.6 ^h	1.6	89.4
Al-TS-2 ^f	9.8	13.7	20.1	14.7	18.3	8.0	38.9 ⁱ	1.3	61.1
ZSM-11 ^f	5.3	4.9	4.3	17.4	4.2	10.6	63.5 ⁱ	1.5	36.5
Silicalite-2	3.3	3.1	7.0	7.7	4.9	7.5	72.9 ^j	1.2	27.1
SiO ₂ ^g	3.7	4.7	8.4	11.1	6.5	9.4	64.6 ^j	1.2	33.4
TS-1 ^f	24.2	79.5	31.4	29.4	17.9	15.6	5.7 ^h	1.8	94.3

^aReaction conditions: catalyst (g) per mole n-C₆=1.76; temp. (K)=373; feed (mol)=n-C₆:H₂O₂=0.116:0.039; solvent=acetone; reaction duration (h)=5.

^bH₂O₂ utilized for monofunctional product formation.

^c2-ol=2-hexanol; 3-ol=3-hexanol; 2-one=2-hexanone and 3-one=3-hexanone.

^d2-/3- ratio=(2-ol+2-one/3-ol+3-one).

^eProduct selectivity=(Σ 2- and 3- compounds/n-hexane reacted)×100.

^fTS-2: Si/Ti=29; Al-TS-2: Si/Ti=70, Si/Al=74; ZSM-11: Si/Al=69; TS-1: Si/Ti=31.

^gFumed silica, type S-5005, supplied by Sigma Chemical, MO, U.S.A.

^hMostly oxygenates with more than one functional group and lactones.

ⁱMethylcyclopentane, benzene, alkylbenzenes and oxygenates.

^jSimilar to i, but with additional unidentified oligomeric material.

TABLE 2

Influence of Ti content of TS-2 on the oxidation of n-hexane^a

Ti/ (Si+Ti)	n-C ₆ Conversion (wt.%)	H ₂ O ₂ ^b utilization (mol%)	Break-up of products (wt.%) ^c					-ol/-one ^d ratio	2-/3- ratio ^e	Product ^f selectivity
			2-ol	2-one	3-ol	3-one	others			
0.033	18.9	61.6	31.0	24.0	17.9	16.5	10.6 ^g	1.2	1.6	89.4
0.014	15.4	47.2	30.3	21.2	19.2	16.1	13.2 ^g	1.3	1.5	86.8
0.008	11.3	33.0	26.1	20.3	23.1	16.0	14.5 ^g	1.4	1.2	85.5
Silicalite-2	3.3	3.1	7.0	7.7	4.9	7.5	72.9 ^h	0.8	1.2	27.1

^aReaction conditions as in Table 1.

^bH₂O₂ utilized for monofunctional product formation.

^c2-ol=2-hexanol; 3-ol=3-hexanol; 2-one=2-hexanone and 3-one=3-hexanone.

^d-ol/-one ratio=Σ alcohols/Σ ketones.

^e2-/3- ratio=(2-ol+2-one/3-ol+3-one).

^fProduct selectivity=(Σ 2- and 3- compounds/n-hexane reacted)×100.

^gMostly oxygenates with more than one functional group and lactones.

^hSimilar to g, but with additional unidentified oligomeric material.

conditions. The results are presented in Table 2. For comparison, the results obtained with silicalite-2 with a Ti/(Ti+Si) ratio ≈ 0 is also included in Table 2. As expected, the activity and selectivity of the catalysts increased with increasing Ti content. However, the increase in activity is not in proportion to the increase in Ti content of the samples if we examine the data obtained

after 5 h (Table 2). The influence of duration of the run on conversion in the case of two different TS-2 samples (with Si/Ti=29 and 124) is presented in Fig. 1 (curves (a) and (c)). It is observed that although conversion increases with time, beyond 3 h the increase is small. Examining Table 2, it is noticed that both the 2-/3- ratio and alcohol/ketone ratio are affected by a change in the Ti content. The increase in -ol/one ratio with decreasing Ti content suggests that Ti ions also catalyze the oxidation of alcohols to ketones.

Influence of concentration of catalyst

Table 3 presents the results of the experiments carried out with different amounts of catalyst. A general trend of increasing conversion and selectivity for monofunctional products with increasing catalyst concentration is noticed, the increase being small beyond a catalyst concentration of 1.7 g per mole n-hexane. Compared to the 2-/3- ratio, the alcohol/ketone ratio is more influenced by an increase in the catalyst amount (Table 3). Figure 1 also

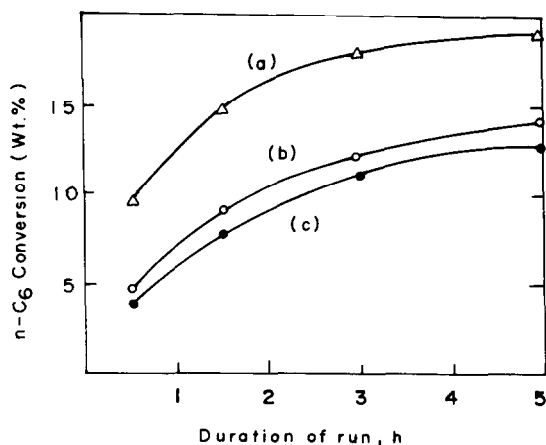


Fig. 1. Influence of duration of run on n-hexane conversion. Temp. (K)=373; n-C₆:H₂O₂ (mole)=0.116:0.039; solvent=acetone. (a) Si/Ti=29, 1.7 g mol⁻¹ n-C₆; (b) Si/Ti=29, 0.9 g mol⁻¹ n-C₆; (c) Si/Ti=125, 1.7 g mol⁻¹ n-C₆.

TABLE 3

Effect of catalyst (TS-2) concentration on the conversion of n-hexane^a

Amount of catalyst (g mol ⁻¹)	n-C ₆ Conversion (wt.%)	H ₂ O ₂ utilization (mol%)	Break-up of products (wt.%)					-ol/one ratio	2-/3- ratio	Product selectivity
			2-ol	2-one	3-ol	3-one	others ^b			
0.9	14.4	43.8	34.6	19.3	18.8	15.3	12.0	1.5	1.6	88.0
1.7	18.9	61.6	31.0	24.0	17.9	16.5	10.6	1.2	1.6	89.4
4.3	19.8	68.1	33.2	26.6	18.6	15.4	6.2	1.2	1.8	93.8
8.6	20.8	73.8	32.1	29.0	18.3	15.7	4.9	1.1	1.8	95.1

^aReaction conditions as in Table 1.

^bMostly oxygenates with more than one functional group and lactones.

depicts the influence of duration of the run on the conversion at two catalyst concentrations (curves (a) and (b)).

The trends reported in Fig. 1 for both the influence of catalyst concentration (curves (a) and (b)) and Ti content (curves (a) and (c)) are in the same expected direction; since only the Ti species are active centers for the reaction, an increase in Ti content leads to a more rapid conversion of n-hexane. However, beyond 3–4 h, H_2O_2 in the mixture is totally depleted and further n-hexane conversion does not take place. The depletion of H_2O_2 is due to both non-selective decomposition (and loss) and selective consumption in the reaction. Blank experiments carried out in both the presence and absence of the catalyst showed that all the H_2O_2 decomposed within a 5 h period. Hence, there is always a competition between reaction and decomposition during the run. When more Ti is present in the system, the reaction rate is enhanced compared to the decomposition rate.

Influence of feed ($n-C_6/H_2O_2$) ratio

While maintaining the concentration of n-hexane constant (0.116 mol), experiments were carried out with three different $n-C_6/H_2O_2$ (mole) ratios. The results are reported in Table 4. Conversion increases with increasing H_2O_2 content, but the product selectivity decreases slightly because of the greater formation of secondary products with more than one functional group. The H_2O_2 utilization is also lower due to greater loss of H_2O_2 by decomposition. As expected, the alcohol/ketone ratio increases with decreasing H_2O_2 content.

Influence of temperature

Experiments carried out at different temperatures (Table 5) suggest the existence of an optimum temperature for maximum yields of the desired products (with a single oxyfunctional group), H_2O_2 utilization and n- C_6 conversion. At high temperatures, n- C_6 conversion and H_2O_2 utilization are low due to H_2O_2 decomposition. At low temperatures, the formation of high-boiling byproducts (not identified in detail) decreases the product selectivity. The alcohol/ketone ratio decreases with temperature. The ratio of 2-/3-

TABLE 4
Influence of concentration of reactants^a

Concentration of reactants (mol)		n- C_6 Conversion (wt.%)	H_2O_2 utilization (mol%)	Break-up of products (wt.%)					-ol/one ratio	Product selectivity
n- C_6	H_2O_2			2-ol	2-one	3-ol	3-one	others ^b		
0.116	0.116	44.5	52.7	22.1	31.5	9.4	25.6	11.4	0.6	88.6
0.116	0.039	18.9	61.6	31.0	24.0	17.9	16.5	10.6	1.2	89.4
0.116	0.023	13.3	68.7	37.8	18.9	21.9	14.3	7.1	1.8	92.9

^aReaction conditions as in Table 1.

^bMostly oxygenates with more than one functional group and lactones.

TABLE 5

Influence of temperature on the selective oxidation of n-C₆ over TS-2^a

Temp. (K)	n-C ₆ Conversion (wt.%)	H ₂ O ₂ utilization (mol%)	Break-up of products (wt.%)					-ol/-one ratio	2-/3- ratio	Product selectivity
			2-ol	2-one	3-ol	3-one	others ^b			
323	5.9	13.1	48.4	7.3	20.7	4.2	19.4	6.0	2.2	80.6
348	11.1	33.8	46.3	15.8	21.6	10.5	5.8	2.6	1.9	94.2
373	18.9	61.6	31.0	24.0	17.9	16.5	10.6	1.2	1.6	89.4
398	17.1	56.9	22.1	24.6	15.6	23.3	14.4	0.8	1.2	85.6

^aReaction conditions as in Table 1.^bMostly oxygenates with more than one functional group and lactones.

TABLE 6

Influence of different solvents on the selective oxidation of n-C₆ over TS-2^a

Solvent	n-C ₆ Conversion (wt.%)	H ₂ O ₂ utilization (mol%)	Break-up of products (wt.%)					-ol/one ratio	2-/3- ratio	Product selectivity
			2-ol	2-one	3-ol	3-one	others ^b			
acetone	18.9	61.6	31.0	24.0	17.9	16.5	10.6	1.2	1.6	89.4
2-butanone	6.0	14.4	12.1	17.1	21.0	18.2	31.6	0.9	0.7	68.2
acetonitrile	12.3	37.8	20.1	9.7	45.9	12.6	11.7	3.0	0.5	88.3
<i>N,N</i> -DMF ^c	3.4	8.0	4.3	15.0	34.6	19.6	26.5	1.1	0.4	73.5

^aReaction conditions as in Table 1.^bMostly oxygenates with more than one functional group and lactones.^c*N,N*-dimethylformamide.

compounds also decreases with temperature, suggesting activation of the 3-position with an increase in temperature.

Influence of solvent

All the above studies were carried out with acetone as solvent. The influence of other solvents on the conversion and product selectivities was also examined, and the results are reported in Table 6. n-C₆ conversion and selectivities (alcohol/ketone ratio and 2-/3- ratio) are influenced by the solvent. The reasons for the solvent effect are probably very intricate, being a function of its polarity, molecular size, counter-diffusion effects in the pores and interaction with the active centers.

Studies on other alkanes

Table 7 reports the results of experiments carried out on different alkanes, which reveal that conversion decreases with increasing carbon number in the case of the alkanes studied (C_n > C₆) [9]. This is attributed to the slower diffusion of the larger molecules into the zeolite channels, which is also apparent from the lower conversion of the bulkier branched hydrocarbon, 3-methylpentane. When equimolar mixtures of n-hexane + 3-methylpentane,

TABLE 7

Reaction of other alkanes and alkane mixtures^a over TS-2^b

Alkane 1 ^c	Alkane 2 ^d	Conversion (wt.%)	
		Alkane 1	Alkane 2
n-C ₆	—	18.9	—
n-C ₇	—	18.2	—
n-C ₈	—	16.5	—
n-C ₁₂	—	13.5	—
n-C ₆	3-MC ₅	7.8	2.8
n-C ₆	2,2-DMC ₄	8.2	1.7
n-C ₆	CyC ₆	12.3	1.8

^aAlkane mixtures = 50 mol.% of each component.^bReaction conditions as in Table 1.^cn-C₆ = n-hexane; n-C₇ = n-heptane; n-C₈ = n-octane; n-C₁₂ = n-dodecane.^d3-MC₅ = 3-methylpentane; 2,2-DMC₄ = 2,2-dimethylbutane; CyC₆ = cyclohexane.

n-hexane + 2,2-dimethylbutane, and n-hexane + cyclohexane are simultaneously reacted, the faster-diffusing n-hexane undergoes reaction preferentially (Table 7).

Conclusions

The titanium silicate molecular sieve TS-2, belonging to the MEL-structure group, is active for the selective oxidation of alkanes in the presence of H₂O₂. As observed in the case of TS-1, oxyfunctionalization of the 2-position in n-hexane is favoured. An increase in the Ti content of TS-2 or its concentration in the reaction mixture increases the selective utilization of H₂O₂ and oxyfunctionalization of n-hexane. H₂O₂ concentration, temperature and nature of the solvent all have an influence on the alcohol/ketone ratio in the product.

Acknowledgements

This work was partly funded by UNDP. JSR thanks CSIR for a Senior Research Fellowship.

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