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Oxidation of propene by molecular oxygen over Ti-modified silicalite catalysts

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Ti-modified high silica zeolite with an Si/Al ratio of 1900 was found to be effective for the oxidation of propene to oxygenates such as propene oxide, in the presence of molecular oxygen at 573 K.

Propylene oxide is an important industrial intermediate which has traditionally been produced by the epoxidation of propene with organic hydroperoxides. In this proress, organic alcohols are stoichiometrically produced as by-products. Recently, titanium silicate-1 (TS-1) zeolite has been shown to be active for the reaction with H_2O_2.[1] This process is still liquid phase whereas the gas phase is more favorable due to product separation. Concerning the gas phase, Haruta and coworkers[2] and Moulijn *et al.*[3] have published work relating to epoxidation with propene/O_2/H_2 over Au dispersed on TS-1 and other Ti-containing supports. In these cases, selectivity to propene oxide is high ($>90\%$), but propene conversion is $<5\%$ and a large amount of H_2 is consumed to form H_2O. Direct propene oxidation by molecular oxygen without H_2 into propene oxide would be of value. The possibility to form propene oxide (PO), in particular, was shown, using $AgNO_3$ or KNO_3 supported on TS-1 and K_2CO_3 or KCl on the same matrix with a PO yield of 0.02%.[4] ARCO Chemical Technology has recently reported improved propene oxide yield in the presence of ethyl chloride.[5] In these cases without gaseous co-reactant such as hydrogen, acidic compounds such as nitrates and chlorides on the catalyst surface could be important for propene activation. In the course of our research program on direct oxidation of propene without any co-reactant, we have reported that titanium sulfate-modified amorphous zirconia was effective for this reaction,[6] although the propene conversion was below 6% and the PO yield only *ca.* 0.5%. Thus, in order to improve propene oxide yield, we tried the use of zeolite families as catalyst supports. In the present study, we report titanium-modified high silica zeolites with different ratios of Si/Al which are effective for the propene oxidation by O_2 without any co-reactant.

High silica zeolite (denoted silicalite) with Si/Al ratio of 3000 was prepared from $Si(OEt)_4$ and tetraethylammonium hydroxide by a hydrothermal method followed by calcination in a air flow at 823 K for 5 h. The other high silica zeolites (denoted HSZ) employed were provided by TOSO Co. Ltd. [HSZ(68),† HSZ(190)† and HSZ(1900)†]. Titanium-modified HSZ samples containing 7.5 wt% Ti[Ti/HSZ(68)] were prepared by the impregnation method.‡ All chemicals were purchased from Wako Pure Chemicals Co.. The amounts of adsorption of ammonia or CO_2 were estimated by using a Thermal Analysis System 001 instrument (MAC SCIENCE Co.).§

The catalytic reaction was performed under atmospheric pressure at temperatures between 473 and 673 K. A tubular fixed-bed reactor (OD = 1.25 cm, length = 60 cm) was filled with 1.0 g of catalyst powder and quartz sand (2.0 g). A pretreatment was done prior to each reaction at 673 K under air flow (25 ml min^{-1}) for 2 h. The reactant feeds were C_3H_6 (7.5 ml min^{-1}) and air (17.5 ml min^{-1}). Hydrocarbons and oxygenated compounds were detected by TCD and FID gas chromatography, the former with Porapack Q (1 m) at 673 K, the latter with 20 wt% FFAP on Chromosorb W (3 m) at 373 K. Products in the gas phase was analyzed by another TCD equipped with a Porapak Q column (3 m) and molecular sieve 5 Å column (3 m) kept at 343 K. The reaction products were also confirmed by mass spectrometry. In order to check the initial activities of catalysts, GC analyses were started 15 min after reaching the reaction temperature. The products were propene oxide (PO), acetaldehyde (AA), C_1–C_8 hydrocarbons (HC), CO and CO_2 (CO_x) and small amounts of other oxygenates [propanal, acetone, formaldehyde, alcohols (MeOH, EtOH, Pr^iOH)] were also detected.

The catalytic performances at 573 K are summarized in Table 1. No product was formed through the reactor in the absence of catalyst. Both Ti/SiO_2 (run 1) and Ti/TiO_2 (run 2) exhibited low propene conversion and only hydrocarbons (HC) and CO_x were produced. For the HSZ family we found that the catalyst

Table 1 Results of the oxidation of propene by molecular oxygen 573 K[a]

Run		Conv. propene (%)	PO yield (%)	Selectivity (%)[d]									
				PO	PA	AA	HA	AL	AC	Alc	HC	CO_x	Residue[e]
1	7.5% Ti/SiO_2	3.76	0	0	0	0	0	0	0	0	72.7	24.7	2.6
2	7.5% Ti/TiO_2	2.11	0	0	0	0	0	0	0	0	47.0	52.9	0.1
3	7.5% Ti/HSZ(68)[b]	97.8	3.11	3.18	5.85	6.25	0	0	0	5.39	44.5	5.12	35.6
4	7.5% Ti/HSZ(190)[b]	95.5	8.90	9.32	9.85	20.0	0	28.3	0	0	31.4	1.13	9.85
5	7.5% Ti/HSZ(1900)[b]	47.7	17.3	36.3	0	29.6	2.64	0.66	0	2.87	27.8	0	0.13
6	7.5% Ti/silicalite(3000)[b]	1.89	Trace	Trace	0	0	0	0	0	0	100	0	0
7	15% Ti/HSZ(1900)[b]	78.2	20.4	26.1	0	23.6	2.92	0	0	2.60	43.9	0.74	0.14
8	15% Ti/HSZ(1900)[bc]	9.03	3.69	40.9	0	23.5	0.12	0	0	0	35.3	0	0
9	HSZ(1900)[b]	83.2	6.60	7.93	0	11.3	1.73	3.43	0.30	5.32	69.1	0.53	0
10	7.5% Ti/HSZ(1900)[be]	37.3	8.81	23.6	0	16.2	0.06	0	0	0	59.7	0.44	0

[a] *Reaction conditions*: see text. [b] Number in parentheses is the Si/Al ratio for the catalyst support employed. [c] Reaction carried out at 523 K. [d] Products propene oxide (PO), acetaldehyde (AA), formaldehye (HA), acrolein (AL), acetone (AC), alcohol [Alc, (MeOH + EtOH + Pr^iOH)], hydrocarbons [HC, ($C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_7 + C_8$)], CO and CO_2 (CO_x). [e] Residue estimated using the equation 100 − sum of all detectable products. Calcination of the catalyst carried out at 173 K.

Table 2 Quantitative estimation of acid and base sites on Ti-modified HSZ catalysts by NH_3- or CO_2-TPD[a]

Sample	Base sites[b]			Acid sites[b]		
	x Within 673 K CO_2(g)/Cat(g)	*y* Within 440 K CO_2(g)/Cat(g)	*y*/*x*[c] (%)	*x* Within 673 K NH_3(g)/Cat(g)	*y* Within 440 K NH_3(g)/Cat(g)	*y*/*x*[c] (%)
7.5% Ti/silicalite(3000)	0.0104	0.0080	76.9	0.0129	0.00956	74.1
7.5% Ti/HSZ(1900)	0.0187	0.0143	76.6	0.0495	0.042	85.3
7.5% Ti/HSZ(68)	0.0196	0.0147	75.0	0.0339	0.0233	68.7

[a] Thermogravimetric analysis conducted in argon in the range 300–673 K. [b] The acid or base sites were estimated by the amounts of NH_3 or CO_2 desorbed within each prescribed temperature. [c] These values, calculated [100 (*y*/*x*)] can be regarded as the percentage of *weak* base or acid sites.

performances were strongly dependent on the Si/Al ratio of the supports. For 7.5% Ti/HSZ(68) (run 3), propene conversion was very high (97.8%) and some oxygenates were produced with CO_x and a substantial amount of residue, but the PO yield was only 3.11%. The 7.5% Ti/HSZ(190) (run 4) also showed high propene conversion of 95.5% and both CO_x and the amount of residue were decreased, while the selectivities to oxygenates were increased. In this case the PO yield was 8.90%.

On the other hand, the conversion of propene on 7.5% Ti/HSZ(1900) was approximately half the propene conversion of 7.5% Ti/HSZ(190), while selectivities to CO_x and residue (0.13%) were dramatically lower than for 7.5% Ti/HSZ(190). For 7.5% Ti/HSZ(1900) (run 5) the selectivity to PO was found to be 36.3% and major by-products were acetaldehyde (AA) and hydrocarbons (HC). As a result, the PO yield (17.3%) on 7.5% Ti/HSZ(1900) was twice that of 7.5% Ti/HSZ(190). 7.5% Ti/silicalite (3000) (run 6), on the other hand, showed much lower propene conversion (1.89%) than 7.5% Ti/HSZ(1900). Therefore, it is indicated that titanium-modified HSZ with an Si/Al ratio of 1900 not only has a moderate ability to activate propene using molecular oxygen, but also properties suitable for predominant formation of oxygenates (in particular, PO) over hydrocarbons (HC).

The 15% Ti/HSZ(1900) catalyst (run 7) exhibited higher propene conversion (78.2%) than 7.5% Ti/HSZ(1900), although the PO selectivity was slightly decreased, while HC selectivity was increased. In this case, the PO yield was 20.4%, >10 times those previously reported under O_2/H_2 conditions[2,3] and, at least, >3 times recently reported for Ag-containing catalyst[4,5] or photocatalyst[7] systems. At 523 K, the PO selectivity on 15% Ti/HSZ(1900) was as high as 40.9%, while the propene conversion was 9.03% (run 8). HSZ(1900) alone (run 9) showed higher propene conversion and HC selectivity than 7.5% Ti/HSZ(1900), while less selectivity to oxygenates was observed. This indicated that surface properties for oxygenate formation were improved by Ti modification.¶

The mechanism of oxidation of propene over Ti/HSZ catalysts is not clear. However, catalyst performances are dependent on Si/Al ratio of the HSZ supports (Table 1) and, therefore, it seems likely that surface acid–base properties are responsible for the catalyst behavior, in particular, propene conversion and residue yield. In fact, as shown in Table 2, where NH_3- or CO_2-TPD was conducted by using thermogravimetric methods, 7.5% Ti/silicalite(3000) catalyst exhibited weaker adsorption for NH_3 as well as CO_2 than the other two catalysts; This is in good accordance with much lower propene conversion of this catalyst relative to the other catalysts (Table 1, runs 3, 5 and 6).

NH_3 adsorption on 7.5% Ti/HSZ(1900) catalyst was slightly larger than that on 7.5% Ti/HSZ(68), while the amount of CO_2 adsorbed was similar (Table 2). However, as much as 85.3% of NH_3 adsorbed on 7.5% Ti/HSZ(1900) was found to be desorbed below 440 K (Table 2, *y*/*x* ratio and Fig. 1), whereas the ratio of NH_3 desorption below 440 K on 7.5% Ti/HSZ(68) was only 68.7%; These findings indicated that the ratio of strong to weak acid sites on 7.5% Ti/HSZ(1900) is smaller than that on 7.5% Ti/HSZ(68). This could be consistent with the fact that the 7.5% Ti/HSZ(1900) catalyst showed lower propene conversion and smaller amounts of residue product than those for 7.5% Ti/HSZ(68) (Table 2, runs 3 and 5). The calcination of 7.5% Ti/HSZ(1900) at 1073 K, higher by 100 K than the standard calcination temperature (973 K), would result in a decrease in weak acid sites, while strong acid sites might still be retained. As a result, propene conversion was decreased to 37.3% and selectivity to hydrocarbon formation (HC) was raised to 59.7% (Table 1, run 10).

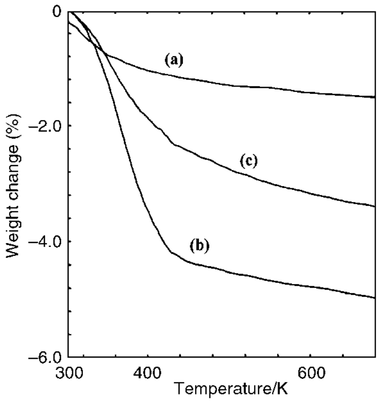

Fig. 1 NH_3-TPD data for (a) 7.5% Ti/silicalite(3000), (b) 7.5% Ti/HSZ(1900) and (c) 7.5% Ti/HSZ(68).

In summary, Ti-modified HSZ(1900) was found to catalyse the oxidation of propene to oxygenates, such as propene oxide, by molecular oxygen at 573 K. The catalyst performances are affected by the Si/Al ratio of the HSZ supports as well as the presence of titanium. Cooperation between moderate acid properties of HSZ(1900) and titanium favors oxygenate formation. It is expected that fine control of acid properties of these supports and titanium content well enhance the catalyst performances for propene oxide formation.

Notes and references

† These zeolites are of H-ZSM-5 type where the number in parentheses is the Si/Al ratio.

‡ The calcined HSZ was evacuated at 673 K for 3 h in order to eliminate a small amount of water. Then, the HSZ was impregnated with $Ti(OPr^i)_4$ in Pr^iOH, followed by addition of H_2O (25 g) leading to precipitation of titanium oxide. The sample was then dried at 373 K for 10 h and finally calcined at 973 K for 3 h.

§ The sample was evacuated at 673 K for 2 h then, after cooling to 373 K, ammonia adsorption on to the surface was allowed to occur to saturation. Evacuation was then applied for 1 h at the same temperature followed by thermal gravimetric (TG) analysis. CO_2 adsorption was carried out at 300 K.

¶ The TS-1 catalyst contains 1.68 wt% Ti and an Si/Al ratio of 46,[1] in contrast to 7.5% Ti and Si/Al ratio of 1900 for 7.5% Ti/HSZ(1900). TS-1 is thus less effective for selective PO formation than 7.5% Ti/HSZ(1900) catalyst under propene/O_2.

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