

Hydroxylation of Benzene and Hexane by Oxygen and Hydrogen over Palladium-containing Titanium Silicalites

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Palladium-containing titanium silicalite zeolites catalyse the hydroxylation of benzene and hexane by O_2-H_2 under mild conditions to give phenol and hexanols, respectively.

The direct introduction of hydroxy groups into an aromatic ring¹ and unreactive alkanes² has been attracting much interest. Titanium silicalite³ is a recently developed new type molecular sieve which incorporates Ti in the framework.⁴ It has been found to be effective in the hydroxylation of aromatic compounds such as benzene⁵ and phenol^{3,6} and also of alkanes^{7,8} by H_2O_2 as an oxidant under mild conditions. Since using molecular oxygen in place of H_2O_2 should have significant advantages, we have sought to establish procedures through which molecular oxygen could be used. We have now designed a system containing Pd metal particles in the titanium silicalite which, in an oxygen-hydrogen atmosphere, should generate H_2O_2 at the palladium site^{9,10} and then use that H_2O_2 to oxidise various organic substrates present in the pore system. We now report hydroxylation of benzene and hexane by oxygen-hydrogen over Pd-containing titanium silicalite catalysts.

A modified synthetic procedure, similar to that claimed in a patent,¹¹ led to aluminotitanium silicalite-1 (ATS-1; Si:Ti = 20, Si:Al = 28). Titanium silicalite-1 [TS-1(A) with Si:Ti = 31 and TS-1(B) with Si:Ti = 130] was prepared according to a method in a patent.¹² ATS-1 and HZSM-5 (Tosoh, Si:Al = 12) were exchanged with aqueous $[Pd(NH_3)_4]Cl_2$. Pd/TS-1(A) was prepared by impregnating TS-1(A) with $PdCl_2$ dissolved in 1 mol dm^{-3} hydrochloric acid. Pd/TS-1(B) was prepared by impregnating TS-1(B) with aqueous $[Pd(NH_3)_4]Cl_2$. The Pd-loaded catalysts were calcined in air at 500 °C and subsequently reduced in hydrogen at 400 °C. Pd/C (NE Chemcat) was reduced in hydrogen at 400 °C. A typical reaction was carried out in a small glass flask fitted with a gas inlet and outlet. Catalyst (50–100 mg), benzene or hexane (10 ml) and 3–30 mmol dm^{-3} hydrochloric acid (5 ml) was placed in the flask and stirred with a magnetic stirrer. The reactant gas mixture ($O_2:H_2 = 14:3$) was bubbled into the liquid at a flow rate of 17 ml min^{-1} at 25 to 40 °C. Catalysts were filtered off and both the organic and aqueous phases were subjected to gas chromatographic analysis.

Pertinent data are shown in Table 1. Hydroxylation of benzene to phenol took place over the ATS-1 and TS-1 catalysts containing Pd in the presence of hydrochloric acid.

No further oxidation products such as hydroquinone, catechol, and benzoquinone were obtained. No reaction occurred over the catalysts without Pd. Although Pd/HZSM-5 was found to be slightly active in the phenol formation, it is clearly seen that Pd-Ti dual functionality resulted in much better catalytic performance. Over the Pd/HZSM-5 catalyst, the hydroxylation seems to be promoted by acid sites; the hydroxylation of benzene by H_2O_2 to phenol in the presence of Lewis acid catalysts is known¹³ and it has been claimed in a patent¹⁴ that HZSM-5 catalyses the hydroxylation of phenol by H_2O_2 .

The rate of benzene hydroxylation over TS-1(A) using 30% H_2O_2 as the oxidant was found to be much higher than that over Pd/TS-1(A) using O_2-H_2 mixture, suggesting that the rate of H_2O_2 formation over the latter was not sufficiently high. Since this was thought to be partly owing to the poor dispersion of Pd metal particles on Pd/TS-1(A) prepared by impregnation with $PdCl_2$, a search was made for the improvement in the method for supporting Pd. Pd/TS-1(B) prepared by impregnation with $[Pd(NH_3)_4]Cl_2$ exhibited improved catalytic performance in terms of turnover number. With this catalyst the hydroxylation rate was sharply dependent on reaction temperature. The decreased rate at 40 °C may be caused by the decrease in the concentration of H_2O_2 formed, since higher temperatures were found favourable when H_2O_2 was used as the oxidant. Lower temperature had a beneficial effect on the concentration of H_2O_2 ,⁹ being supportive of this temperature dependence. Sulfuric acid was able to substitute for hydrochloric acid. They are known to be required additives to form H_2O_2 from O_2 and H_2 on Pd catalysts.⁹ Whereas NaCl was slightly effective, no oxidation product was obtained without such ionic additives.

A physical mixture of Pd/C and TS-1 turned out to be active when a cosolvent such as Bu^tOH was added. Without cosolvent hydrophobic Pd/C was present in the organic phase, resulting in difficult contact with the aqueous phase, where H_2O_2 formation should take place.

These Pd-Ti systems were active in the oxidation of other substrates such as alkanes, alkenes and alcohols. Hexane was hydroxylated into hexan-2- and -3-ols, which were further

Table 1 Oxidation of benzene and hexane with O₂-H₂^a

Reactant	Catalyst ^b	Aqueous phase/ mmol dm ⁻³	Oxidation products ^{c/} μmol	Turnover	
				(mol/mol-Ti)	(mol/mol-Pd)
Benzene	Pd(3.1)/ATS-1 ^d	HCl 30	96	1.3	3.3
	Pd(5.9)/HZSM-5 ^d	HCl 30	3.8	—	0.069
	Pd(5.2)/TS-1(A) ^d	HCl 30	29	0.59	0.59
	TS-1(A) ^d	H ₂ O ₂ 30%	255	4.9	—
	Pd(0.5)/TS-1(B)	HCl 30	15	2.3	6.6
	Pd(1.4)/TS-1B	HCl 30	33	5.2	5.2
	Pd(1.4)/TS-1B ^e	HCl 30	85	13.5	13.5
	Pd(1.4)/TS-1B ^f	HCl 30	52	8.3	8.3
	Pd(1.4)/TS-1B ^f	HCl 10	59	9.4	9.4
	Pd(1.4)/TS-1B ^f	H ₂ SO ₄ 5	55	8.9	8.9
	Pd(1.4)/TS-1B ^f	NaCl 10	10	1.6	1.6
	Pd(5.0)/C ^g + TS-1(A) ^d	HCl 30	2.5	0.049	0.024
	Pd(5.0)/C ^g + TS-1(A) ^d	HCl 30 ^h	65	1.3	0.63
	Hexane	Pd(1.4)/TS-1(B) ^f	HCl 30	2.0	0.32
Pd(1.4)/TS-1(B) ^f		HCl 3	2.3	0.53	0.53
Pd(1.4)/TS-1(B) ^f		HCl 3 ⁱ	7.4	1.2	1.2

^a Conditions: reactant 10 ml, water 5 ml, O₂ 14 ml min⁻¹, H₂ 3 ml min⁻¹, 25 °C, 3 h. ^b Shown in parentheses is wt% of Pd; ATS-1; Si:Ti = 28; ZSM-5; Si:Al = 12; TS-1(A); Si:Ti = 31; TS-1(B); Si:Ti = 130. 0.05 g of catalyst used unless otherwise stated. ^c Phenol from benzene; hexan-2-ol, hexan-3-ol, hexan-2-one and hexan-3-one from hexane. ^d 0.10 g. ^e 35 °C. ^f 40 °C. ^g 0.22 g. ^h Bu⁴OH 5 ml added. ⁱ MeOH 1 ml added.

oxidized in part to the corresponding ketones. In this case the product turnover was sensitive to the concentration of HCl, as shown in Table 1. The addition of MeOH was effective as in the case of oxidation by H₂O₂ over TS-1.⁷ Finally we note that shape selectivity was found in the oxidation of alkanes and alkenes similar to that observed for the oxidation where H₂O₂ was used as oxidant;^{7,15} the rates for oxidation of cyclic alkanes and alkenes were much lower than those of linear alkanes and alkenes.

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