

Zeolite-catalysed Selective Decomposition of Cumene Hydroperoxide into Phenol and Acetone†

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Crystalline, microporous molecular sieves efficiently catalyse the selective decomposition of cumene hydroperoxide into phenol and acetone, both under batch (25 °C) and down-flow fixed-bed (60 °C) conditions; large-pore high-silica zeolites, mainly zeolite Beta and its metallo-silicate (B-, Fe- and Ga-silicate) analogues, are found to be particularly useful catalysts in this reaction giving $ca. 92 \pm 3\%$ phenol selectivity.

Owing to their Brönsted acidity, shape selectivity and thermal stability, crystalline microporous aluminosilicates, commonly known as zeolites, have been extensively used as environmentally friendly heterogeneous catalysts in a variety of organic transformations.^{1,2} Phenol is an industrially important chemical generally produced *via* acid-catalysed decomposition of cumene hydroperoxide.³ Various Brönsted and Lewis acids in homogeneous systems^{4–7} at 0–50 °C and cation exchange resins in pseudo-heterogeneous systems^{8–10} have been reported as catalysts for cumene hydroperoxide decomposition. Phenol selectivity in the presence of an acid catalyst such as sulfuric acid was in the range 95–98% with more than 99% conversion.¹¹ Commercially, the concentrated cumene hydroperoxide (CHP) solution is cleaved in the presence of sulfuric acid catalyst, the phenol yield being 95–98% mol%. The cleavage effluent, containing the acid used as catalyst as well as formic and acetic acids, formed as by-products, has to be neutralized and extracted to avoid corrosion and environmental problems.¹²

Now we report, for the first time, an efficient catalytic conversion of cumene hydroperoxide into phenol and acetone using solid zeolite catalysts under heterogeneous liquid-phase conditions both in a batch and fixed-bed reactor system at between room temperature and 60 °C.

Experimental

In a typical batch experiment, to a solution of cumene hydroperoxide (2 g; 20% solution in cumene) in a 50 ml round bottomed flask was added the zeolite catalyst (0.2 g), obtained according to a known literature procedure.^{13–16} After completion of the reaction, the solid catalyst was filtered off before the products were analysed. In a fixed-bed down-flow reactor system, the H-form of the catalyst (zeolite Beta) was made into pellets (20–30 mesh size), and the binder-free zeolite (1 g anhydro.) was loaded at the centre of the down-flow silica-reactor (1 cm i.d., 30 cm length) using porcelain beads as the inert material. Cumene hydroperoxide (20% solution in cumene; 2 ml h⁻¹) along with carrier gas nitrogen (40 ml min⁻¹) was fed through a syringe pump (Sage Instruments, USA). The reactor temperature was maintained by an electrical heater. The products were analysed by capillary gas chromatography (HP-5880, using FID detector).

Results and Discussion

Table 1 indicates that the reaction was completed within 5 min at 25 °C and the phenol selectivity was $90 \pm 2\%$ in all the cases where zeolite Beta analogues were used as catalyst (entries 1–4). Entries 2–4 suggest that not only aluminosilicate zeolites but their Fe, Ga or B analogues can also be effectively used as catalyst. The phenol selectivity is slightly higher for Fe, Ga and B-Beta samples. Zeolite ZSM-5

Table 1 Catalytic decomposition of cumene hydroperoxide over various zeolites

Entry	Zeolite	SiM Ratio ^a	T ^b /°C	Reaction time/min	Conversion mass%	Phenol selectivity mol%
1	H-[Al]-Beta	14	RT	5	100	88.0
2	H-[Ga]-Beta	20	RT	5	100	92.0
3	H-[Fe]-Beta	22	RT	5	100	91.0
4	H-[B]-Beta	30	RT	5	100	92.0
5	H-[Al]-ZSM-5	30	RT	5	100	86.0
6	H-[Ga]-ZSM-5	35	RT	5	100	88.5
7	H-[Fe]-ZSM-5	30	RT	5	100	88.0
8	H-Mordenite	7.0	RT	5	100	86.5
9	H-Y	2.5	40	10	96.0	85.0
10	H-[Al]-ZSM-12	40	40	30	95.0	82.0
11	H-[Al]-NCL-1	40	40	15	85.0	83.5
12	H-[Al]-ZSM-22	60	40	15	65.0	87.5
13	H-[Al]-MCM-22	30	40	15	90.0	87.0
14	H-[Al]-ZSM-48	50	60	60	45.0	80.0
15	H-[Al]-EU-1	50	60	30	80.0	88.7
16	H-SAPO-5	—	60	60	10.0	88.0
17	H-AIPO-5	—	60	60	25.0	86.0
18	H-[Al]-Beta ^c	14	60	60	99.0	95.0
19	No catalyst	—	—	—	—	—

^aM = Al, Ga or Fe. ^bRT = room temperature. ^cFixed bed reaction: temperature = 60 °C, catalyst = H-Beta (1 g), feed rate = 2 ml h⁻¹, carrier gas = nitrogen (40 ml min⁻¹). Products were collected after 1 h. Mordenite and H-Y zeolites were obtained from Degussa, other catalysts were prepared according to the corresponding referenced method. The selectivity of phenol was confirmed by GC-5880 using a capillary column. The other products include quinones, catechol, acetophenone and higher boiling products such as α -methylstyrene and α -cumylphenol.

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(entries 5–7) and Mordenite (entry 8) are also quite efficient catalysts. However, with these catalysts the phenol selectivity is slightly lower (86–88.5%) compared to that exhibited by Beta zeolites (88–95%). Over zeolite Y (entry 9), the conver-

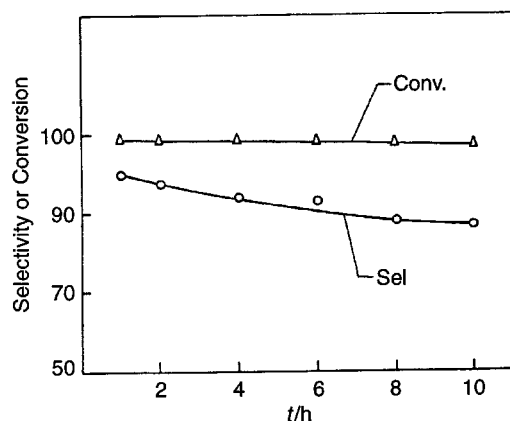


Fig. 1 Decomposition of cumene hydroperoxide into phenol and acetone over zeolite Beta (Si/Al = 14): temperature = 60 °C, LHSV, 2 h⁻¹; Conv = cumene hydroperoxide conversion, mol%; Sel = phenol selectivity, mol%

sion was slightly less (96%) and the phenol selectivity was ca. 85%. However, over ZSM-12,¹³ NCL-1,¹⁴ ZSM-22,¹³ EU-1,¹³ MCM-22¹⁵ and ZSM-48¹³ (entries 10–15), lower conversions as well as selectivities were obtained. Medium-pore zeolites with unidimensional channels, such as ZSM-22, ZSM-48 and EU-1, exhibit lower conversions and selectivities due to diffusional restrictions imposed by the channel system of these zeolites on the reactant and products. However, large-pore unidimensional zeolites, such as ZSM-12, NCL-1 and MCM-22, show ca. 85–90% conversion and selectivity. Entries 16 and 17 show the conversions and selectivities of cumene hydroperoxide over AlPO₄-5¹⁶ and SAPO-5¹⁷ molecular sieves. Unlike aluminosilicates with strong Brönsted acidity, aluminophosphates (neutral) and silicoaluminophosphates (weak Brönsted acidity) exhibit lower activity in the cumene hydroperoxide decomposition, clearly suggesting the requirement of strong Brönsted acid-sites for the decomposition of cumene hydroperoxide into phenol and acetone.

The above results indicate that strong Brönsted acid sites are needed for this reaction. Since Beta, ZSM-5 and Morde-nite possess stronger acid sites compared to zeolites like Y, ZSM-22, ZSM-48, etc.,^{18,19} the conversion is complete using the former. Furthermore, with the reaction being quite fast, the quick diffusion of the reactants into the zeolite channels and of the products from the zeolite channels (as is the case of zeolite Beta with three-dimensional 12-membered-ring large-pore channels) will reduce the formation of secondary products such as quinones, α -methylstyrene, catechol, etc. and also the small amount of acetophenone. Hence it may be stated that a combination of strong Brönsted acid sites and large pore intersecting channels in a high silica zeolite catalyst is suitable for this reaction.

Entry 18 exhibits the results obtained using a fixed-bed, down-flow reactor giving 95% phenol selectivity at 99% con-

version. The advantages of fixed-bed reaction conditions are: (i) there is no need to separate the solid catalyst from the products and (ii) higher phenol selectivities are obtained. These preliminary studies under unoptimised reaction conditions suggest the feasibility of the use of solid catalysts to replace environmentally hazardous mineral acids like sulfuric acid catalysts in CHP cleavage.

Since under fixed-bed conditions the deactivation of the catalyst with time-on-stream is an important parameter, the effect of time-on-stream on activity and selectivity for the decomposition of cumene hydroperoxide into phenol and acetone under fixed-bed conditions using H-Al-Beta catalyst was studied (Fig. 1). The time-on-stream data show that over 10 h, while the conversion remained the same (at ca. 99%) the phenol selectivity decreased slightly from ca. 95 to 90%. The successful use of a zeolite catalyst is thus demonstrated for the first time. Another advantage is that the zeolite can be regenerated *in situ*, regaining the initial activity and selectivity.

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