Production of Hydrogen Cyanide by the Ammonia Reforming of Toluene

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Summary HCN can be produced from toluene and ammonia in the presence of hydrogen faujasite zeolites at high temperature

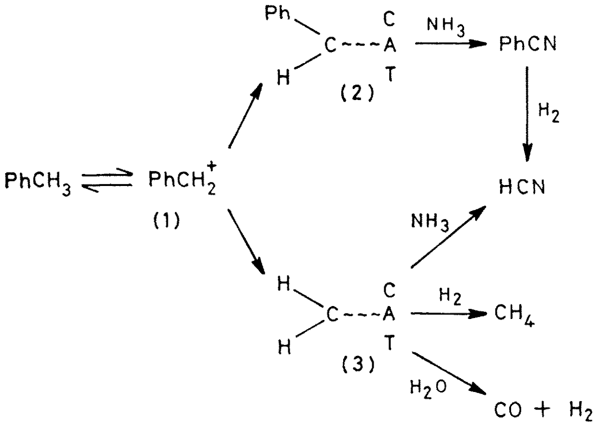
Toluene can be 'reformed' to either benzene and a one-carbon fragment (equation 1) or completely hydrogenated to one-carbon fragments (equation 2) The reagents used have been hydrogen, yielding methane (a),[1] or water giving synthesis gas (b)[2] Considering ammonia as the nitrogen analogue of water, ammonia reforming of toluene should lead to hydrogen cyanide, the nitrogen analogue of carbon monoxide (c) Kaimo[3] has produced HCN and benzene from toluene using a Pt catalyst at temperatures over 1200 K Toluene decomposes thermally to benzene and methane under these conditions, and the methane could be the source of the carbon for HCN We have found that hydrogen faujasites catalyse hydrogen cyanide formation from toluene and ammonia at one atmosphere and somewhat lower temperatures by both equations (1c) and (2c)

	(a)	(b)	(c)	
$PhMe + X \rightarrow PhH + Z$	all[a]	725[a]	905[a]	(1)
$PhMe + X \rightarrow Z$	all[a]	710[a]	940[a]	(2)

(a) $X = H_2, Z = CH_4$
(b) $X = H_2O, Z = CO + H_2$
(c) $X = NH_3, Z = HCN + H_2$

[a] Temperature above which the reactions are thermodynamically possible/K

For example, passing a 4:1 NH_3 toluene mixture over ultrastable HY zeolite (Linde 33-411) at 1000 K with a contact time of 4 s at one atmosphere results in a 100% conversion of toluene by equation (1c) Under these conditions, yields were 80% HCN, 90% benzene, 4% benzonitrile, and 6% coke after 1·5 h on stream Shorter contact times result in lower toluene conversions, and extrapolating to zero conversion shows that HCN is formed both by sequential formation of benzonitrile[4] and subsequent catalytic hydrodecyanation,[5,6] and by a direct path that does not involve benzonitrile The ratio of these paths is temperature- and catalyst-dependent High temperature and a dehydrogenation component in the catalyst favour the direct route The path *via* benzonitrile is favoured by acidic catalysts such as HY, but even in the most favourable case only 60% of the HCN is produced *via* benzonitrile. At complete conversion, higher boiling by-products such as toluonitriles, stilbenes, diphenylmethanes, and diphenylacetylenes amount to about 10% of the benzonitrile recovered.



SCHEME

By analogy with the mechanism for catalytic reforming by hydrogen and water,[1,2,7] the Scheme is proposed to account for the observations. α-Elimination of either benzene or hydrogen may leave a surface-bound carbenoid species (**2**) or (**3**) that is susceptible to nucleophilic attack on hydrogenolysis. Stilbene and diphenylacetylene could come from (**2**),[7] while toluonitriles and diphenylmethane could come from (**1**).[8]

Further support for a species such as (**3**) was obtained by heating a sample of HY, which had been impregnated with benzyl alcohol, in an ammonia atmosphere and monitoring the gases formed. The aromatic portion desorbed at 500 K (benzene : toluene = 10 : 1), while HCN is formed above 900 K only. HCN evolution persists for several hours with no additional source of carbon.

As the temperature is raised, the ratio of HCN to benzene in the product increases and at 1125 K toluene is converted into HCN according to equation (2c). Faujasites are the preferred catalysts because of their thermal stability,[9] but even high surface area aluminas give rise to some HCN. For example, passing a 4 : 1 NH_3 : toluene mixture over HY at 1 atm with a contact time of 3 s after 0·5 h on stream at 1125 K gives an exit gas containing 25% HCN. Approximately 25% of the carbon that was fed remained on the catalyst as coke and N_2 and CH_4 were the major volatile by-products.

Studies of the toluene reactions producing HCN and H_2 may be useful as models for the more well known reactions producing synthesis gas.

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