Direct Amination of Ethylene by Zeolite Catalysis

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Formation of ethylamine by addition of ammonia to ethylene is catalysed by acidic zeolites such as H-Y, H-mordenite, and H-erionite.

Traditional routes for large scale production of lower alkylamines entail reaction of an alcohol with ammonia in the presence of either acidic or supported metal catalysts.[1] Moreover, with the exception of methanol, lower alcohols are typically obtained industrially by hydration of the corresponding alkene.[2] Direct conversion of ethylene into a mixture of ethylamines has been achieved only by treatment with alkali metal amides.[3] We now report the first acid-catalysed amination of ethylene to ethylamine.

At 370 °C and an absolute pressure of 5.5×10^3 kPa, thermal uncatalysed amination of ethylene in a Vycor-filled stainless steel tubular reactor at a total flow rate of 2×10^{-1} dm^3 min^{-1} (mole ratio of ammonia:ethylene 4:1) was <0.05%, based on ethylene. However, when various zeolites in their acidic forms were evaluated, significant catalysis was observed (Table 1). Highest activities were obtained with small to medium pore acidic zeolites, such as H-clinoptilolite, H-erionite, and H-offretite. Na-Y and Na-offretite, sodium ion-exchanged zeolites, and amorphous silica alumina were ineffective as catalysts for ethylene amination.

Activity of zeolites as catalysts for ethylene amination results from the highly acidic nature of proton-exchanged zeolites. At room temperature, ethylene is reversibly adsorbed by acidic zeolites.[4] Changes in the i.r. frequencies of acidic surface hydroxy groups during this process are indicative of hydrogen bonding. Formation of a π-complex between

Table 1. Catalysis of ethylene amination.

Catalyst (g used)	% Conversion at 370 °C	% Selectivity Ethylamine	% Selectivity Diethylamine
None	<0.05		
H-Y (5)	9	87	13
H-mordenite (5)	6	91	9
H-offretite (5)[a]	12	94	6
H-clinoptilolite (5)	14	93	7
H-erionite (5)	11	87	13
H-chabazite/ H-erionite (2.5/2.5)	11	94	6
Na-Y (5)	<1	100	
Na-offretite (5)	<1	100	
Silica alumina (5)	<1	100	

[a] Evaluated at 360 °C.

the surface hydroxy group and ethylene has been implicated as the mechanism of ethylene chemisorption.[4] At elevated temperatures, reaction of the π-complex with ammonia, either adsorbed on the catalyst surface or from the gas phase, forms the adsorbed amine. Subsequent product desorption would regenerate the catalytic site. The necessity of strongly acidic sites and thus of a protonated ethylene intermediate, for catalytic amination is demonstrated by the negligible activity of the non-acidic sodium ion-exchanged offretite and Y zeolites and the weakly acidic amorphous silica alumina.

Despite the high reaction temperatures employed, selectivity to both total amine products, and specifically to ethylamine, is high. This high selectivity appears to result from inclusion of a stoicheiometric excess of ammonia, since selectivities to ethylamine show no dependence on zeolite structure. During the 24 h evaluation period for each catalyst, material accountability across the reactor was excellent. The total feed rate and effluent flow were identical within the limits of experimental error. In addition, no detectable carbon was deposited, as determined by thermogravimetric analysis of the used catalyst.

In summary, we have demonstrated the first acid-catalysed amination of ethylene to ethylamine. Application of this chemistry to substrates such as 2-methylprop-2-ene which form stable cationic intermediates under acidic conditions may provide novel routes to useful amine products.

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