Ammoxidation of Ethanol to Acetonitrile over Molecular Sieves[†]

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For the first time, we report the ammoxidation of ethanol over crystalline, microporous silica-aluminophosphate and Y zeolite with >99.0 and 40.0% m/m yields of acetonitrile respectively.

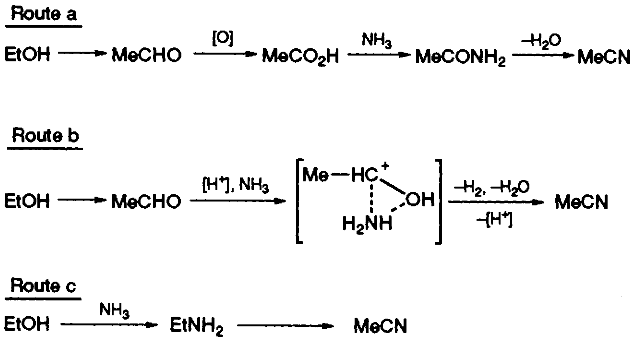
The crystalline, uniform porous silico-aluminophosphates (SAPO) are novel and new catalytic materials.[1] These molecular sieves are used for butane-cracking,[1] amination of carbon monoxide[2] and recently V-APO-5 for the oxidation[3] of toluene. Here, for the first time, we report the selective oxidation and ammoxidation of ethanol to acetaldehyde and acetonitrile in one step over SAPO molecular sieves. Acetonitrile is synthesized by the dehydration of acetamide,[4] catalytic dehydrogenation of triethylamine[5,6] and from ethanol over Sb-V-P-O/Al_2O_3.[7]

SAPO was synthesized using $Al_2(SO_4)_3$, H_3PO_4 and tetrapropylammonium bromide as a template and was a SAPO-40 type. NaY was supplied by PQ Corporation. 10% m/m V_2O_5 was impregnated in SAPO and NaY in aqueous medium and designated as V-SAPO and V-NaY respectively. The XRD patterns and IR spectra indicated the presence of good crystalline material. The reaction was carried out using a down-flow, fixed-bed Pyrex reactor of 12 mm diameter. The reaction was carried out in the temperature range 250–420 °C and the amount of catalyst was 4 g. The weight hourly space velocity (WHSV) was 0.5 h^{-1} and ethanol to water ratio in the feed was 1 : 1 (v/v). The products were analysed by gas chromatography using 5% SE-30 column and confirmed by mass spectrometry and NMR.

Table 1 Formation of acetonitrile from ethanol over molecular sieves[a]

Catalyst	Time on stream/h	Conversion of ethanol (% m/m)	Yield of acetonitrile (% m/m)	Yield of acetaldehyde (% m/m)
SAPO[b]	4	100.0	99.0	—
V-SAPO	1	94.4	83.0	11.1
NaY	(1 + 2)	36.4	36.4	—
V-NaY	4	44.0	44.0	—

[a] *Conditions:* reaction temp. 350 °C, ethanol : water 1 : 1 by volume (in feed), catalyst 4.0 g; WHSV = 0.5 h^{-1} ethanol : NH_3 1 : 5 (mol), O_2 flow rate 30 ml min^{-1}. [b] Air (for O_2) was used.



Scheme 1

Table 2 Reactions over SAPO catalyst[a]

Reactants	Reaction temp./°C	Conversion (% m/m)	Products (yield % m/m)
EtOH + NH_3 + O_2	350	100.0	MeCN (>99.0)
EtOH + O_2	350	52.0	MeCHO (52.0)
EtOH + NH_3	350	51.0	$EtNH_2$ (40.0), MeCHO (10.0)
$EtNH_2$ + O_2	420	78.0	MeCN (32.0)
$MeCO_2H$ + NH_3	420	55.0	MeCN (55.0)

[a] *Reaction conditions.* Catalyst 4 g; WHSV = 0.5 h^{-1}, reactant: H_2O in feed 1 : 1 (v/v);

The reaction of ethanol with ammonia in the presence of oxygen (air) was carried out over SAPO, V-SAPO, NaY and V-NaY as given in Table 1. The temperature was varied from 250° to 420 °C. The highest yield of acetonitrile obtained was >99.0% m/m over SAPO catalyst at 350 °C. The results also show the negligible effect of vanadium impregnation over the formation of acetonitrile from ethanol. The tetrahedral phosphate group is responsible for the mild and selective oxidation of ethanol; Brønsted acidic centres formed owing to the Si–O–Al linkages are responsible for the dehydrative amination.

Three routes in the formation of acetonitrile are shown in Scheme 1. To propose the reaction mechanism based on the product distributions, various reactions were carried out over SAPO catalyst and the products formed are given in Table 2. In case of route a, MeCHO, MeCOOH should be formed as intermediates in absence of ammonia. We have observed only MeCHO in high yield in the presence and absence of air/O_2 from ethanol over SAPO; $MeCO_2H$ was absent as a product which indicates the possibility of route b and not route a.

The reaction of ethanol with ammonia in absence of air at 350 °C over SAPO leads to the formation of ethylamine (>40.0% m/m). The reaction of ethylamine over SAPO gives acetonitrile, as given in Table 2. Thus, route c in Scheme 1 is also valid over SAPO catalyst. In summary, crystalline, uniform porous silico-aluminophosphate molecular sieves, even without elements like Ti and V, are highly active in selective mild oxidation and ammoxidation reactions.

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