Selective Ethane Ammoxidation to Acetonitrile on Alumina-supported Niobium–Antimony Oxides

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Acetonitrile can be synthesized from ethane by heterogeneous catalytic ammoxidation using Nb–Sb mixed oxides supported on alumina; a new type of (amm)oxidation active site on the catalyst, which can lead to a selective insertion of O–N atoms on the double bond of the intermediate ethylene is suggested.

Owing to the unreactive nature of light (C_2–C_6) alkanes, their selective transformation presents several practical difficulties and the only commercial example is the oxidation of n-butane to maleic anhydride.[1] However, because of their widespread availability and low cost, considerable academic and industrial effort is being directed towards the development of new processes based on alkane feedstocks. Vanadyl pyrophosphate is the only solid catalyst that can effectively give selective oxyfunctionalization of an alkane; this catalyst selectively oxidizes C_4 and C_5 alkanes, but is not selective in the oxidation of C_2 and C_3 alkanes.[2]

It has recently been shown that propane can be selectively ammoxidized to acrylonitrile using V–Sb–Al mixed oxides,[3–5] indicating the possibility of developing a new economical process for synthesis of acrylonitrile to replace the conventional process from propene. An analysis of the mechanism and kinetics of the reaction indicates the intermediate formation of propene by oxidative dehydrogenation followed by transformation to acrylonitrile through an allylic ammoxidation mechanism similar to that of conventional catalysts for the transformation of propene to acrylonitrile.[6] This catalytic system, however, is not effective in the selective transformation of ethane, even though ethylene is formed from ethane with some selectivity. The selective transformation of the ethylene intermediate to acetonitrile or acetic acid would not only form more valuable products, but also molecules (especially the former) which are more stable towards oxidation and degradation to carbon oxides, thus allowing higher selectivities to be obtained at higher alkane conversions. The absence of allylic hydrogen atoms in ethylene compared to propene, however, requires a different mechanism for O–N insertion for the selective conversion of the intermediate alkene to more valuable and stable products. In addition to the specific case of the Ag–Al_2O_3 system for ethylene epoxidation, relatively few catalytic systems are known to be capable of selective O–N insertion on ethylene[7,8] and no examples at all of catalytic systems able to functionalize ethane selectively.

In this communication we show how the use of a catalyst based on Nb–Sb mixed oxides supported on Al_2O_3 allows selective ammoxidation of ethane to acetonitrile, through the probable intermediate formation of ethylene. Acetonitrile is a byproduct of the catalytic ammoxidation of propene and ammonia to acrylonitrile, and therefore it is relatively easily available. It is used as a solvent owing to the inherent difficulty in activating it, which has also limited its utilization as a chemical intermediate. However, the possibility of its selective transformation to useful products, such as acrylonitrile by reaction with methanol[9] or glycolonitrile[10] (intermediate in the manufacture of nitrilotriacetic acid or of the amino acid serine) and glycolamide[10] by oxidation on V-oxide in the presence or absence of water vapour, has been shown. Therefore, there may be some interest in the development of a specific process for acetonitrile synthesis using a low-cost feedstock such as ethane.

In addition, the reaction mechanism suggested to explain the results observed involves the direct insertion of O–N on the π-bond orbitals of ethylene to form an intermediate that evolves to acetonitrile. If correct, this mechanism indicates the presence of a new type of selective oxidation functionality in the Nb–Sb–O/Al_2O_3 system. An electrophilic attack of oxygen species, in fact, is usually considered not to be selective,[11] leading only to C–C bond rupture and CO_x formation, whereas it is assumed that selective insertion of O–N requires a nucleophilic attack.[11] Only in the case of Ag/Al_2O_3 does the attack by adsorbed electrophilic oxygen species occur on the electron-rich region of ethylene to form ethylene oxide selectively,[12] but both the nature of the catalyst–reaction products and the range of reaction temperatures (around 200 °C) are very different from those observed in the selective ammoxidation of ethane to acetonitrile on Al_2O_3-supported Nb–Sb oxides.

The Al_2O_3-supported Nb–Sb oxide catalyst was prepared by a slurry method, which involves refluxing Sb hydroxide (obtained by precipitation with ammonia from an aqueous $SbCl_5$–HCl solution), Nb_2O_5 and Al_2O_3 in an ammoniacal solution for 24 h. The Nb : Sb atomic ratio in the solution was 1 : 5 and the amount of Al_2O_3 70% by weight. The solid was then separated by filtration, washed, dried at 150 °C for 24 h, and calcined in air at 620 °C for 6 h (with an intermediate step at 400 °C for 12 h). The chemical analysis of the sample confirms that the Nb : Sb atomic ratio in the final catalyst is equal to that of the starting solution. The surface area of the sample is 233 $m^2\ g^{-1}$ and does not change after the catalytic tests. X-Ray diffraction characterization of the structure of the catalyst indicates the presence of only an amorphous phase, whereas in a similar sample prepared in the absence of Al_2O_3 the presence of α-Sb_2O_4, and Nb_2O_5 could be detected as well as the $SbNbO_4$ rutile phase, even though the presence of the latter is not clear because its diffraction lines are partially masked by the diffraction lines of the former phases.

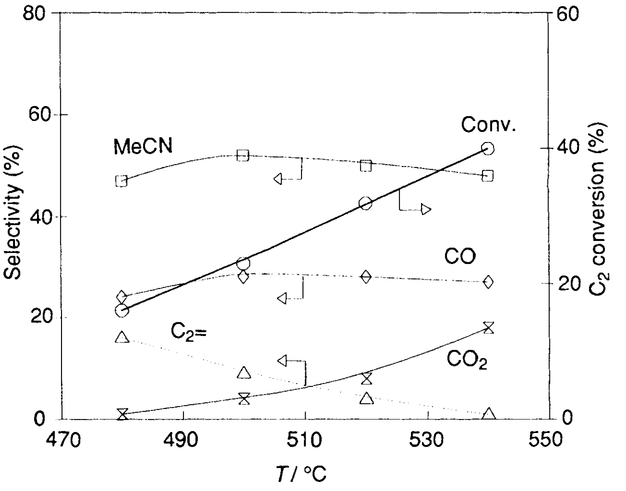

Fig. 1 Ethane ammoxidation to acetonitrile on Al_2O_3-supported Nb–Sb oxide

Catalytic tests were performed at atmospheric pressure in a tubular fixed-bed quartz flow reactor with an axial thermocouple sliding inside to check the isothermal axial profile. A 5 mm copper bar external to the reactor allowed a uniform temperature to be maintained in the reactor. The catalyst sample (3 g) was utilized in particles with dimensions in the 0.2–0.4 mm range diluted with quartz particles in order to avoid hot-spot phenomena and mass–heat diffusional limitations. The absence of such effects was checked by both calculation and experimental verification.

Analysis of both reagents and products was carried out using two on-line gas chromatographs equipped with flame ionization or thermoconductivity detectors for the analysis of organic products and of gases, respectively. Ammonia conversion and HCN formation were determined by absorption in suitable solutions and subsequent titration.[4]

The feed composition for the catalytic tests was 3.6% ethane, 5.9% oxygen, 2.2% ammonia and 88.3% helium. The space-velocity was 457 g h (mole of ethane)$^{-1}$. The catalytic tests refer to steady-state behaviour; no deactivation was observed over about 20 h time-on-stream.

Reported in Fig. 1 is the catalytic behaviour of Al_2O_3-supported Nb–Sb oxide in ethane ammoxidation. Ethane is selectively converted to acetonitrile, with selectivities of the order of 50% at relatively high ethane conversions. In addition to acetonitrile, CO is also formed and the trend of the selectivity to CO against conversion parallels that of MeCN, suggesting that they are formed from a common intermediate. Ethylene (C_2=) is also detected at low reaction temperatures, but its selectivity rapidly decreases with increasing ethane conversion, suggesting the consecutive transformation to acetonitrile and CO. At higher reaction temperatures, CO_2 probably is also formed through a different route from that for CO formation. The HCN selectivity, in contrast, is relatively constant (about 5%).

The same Nb–Sb-based catalyst is also active in propane ammoxidation to form acetonitrile with similar selectivities as from ethane. The formation of CO parallels that of acetonitrile; the molar amounts of acetonitrile and CO are nearly the same in the temperature range investigated, 480–520 °C, and correspond to propane conversions in the 10–30% range.

This confirms that acetonitrile and CO are derived from a common intermediate, as suggested by the ethane experiments. Also, the formation of the corresponding alkene (propene) from propane is detected at lower reaction temperatures and propane conversions. The direct ammoxidation of propene on the same catalyst gives comparable results. The alkene is only slightly more active than the alkane, indicating the high rate of oxidative dehydrogenation of Nb–Sb-based catalysts. Acetonitrile and CO are the main products from the ammoxidation of propene and are formed in similar molar quantities.

Under comparable reaction conditions, V–Sb mixed oxides on Al_2O_3 selectively convert propane to acrylonitrile,[4,5] but the ammoxidation of ethane leads mainly to the formation of carbon oxides. It should also be noted that for V–Sb-based catalysts the order of reactivity is propane > ethane, whereas in the similar system based on Nb the order is ethane > propane which again indicate the specificity of the Nb–Sb oxide on Al_2O_3 system and the presence of specific sites able to form acetonitrile selectivity.

Catalytic data on ethane ammoxidation on Nb–Sb-based catalysts, in agreement with the results for C_3 hydrocarbon conversion, suggest that the formation of the corresponding alkene is the first step in the alkane transformation. On the other hand, this is plausible in terms of a selective mechanism of transformation. For n-butane oxidation to maleic anhydride on a VPO system[1] and for propane ammoxidation to acrylonitrile on V–Sb oxides on Al_2O_3,[4,5] the intermediate formation of the corresponding alkenes was also demonstrated. It is thus reasonable to assume that ethylene is formed from ethane as the first step of the reaction.

More difficult to explain is the consecutive mechanism for the formation of acetonitrile from the intermediate ethylene. It should be noted, however, that propane or propene ammoxidation on the same catalyst does not form acrylonitrile (as found for the V–Sb-based system), but rather forms equimolecular amounts of acetonitrile and CO. This suggests possible electrophilic oxygen attack on the double bond of propene to form a propene oxide-like intermediate. Activated ammonia reacts with this intermediate forming formaldehyde and ethylamine, which owing to the severe reaction conditions, are immediately transformed to the more stable products, CO and acetonitrile. Similarly, the oxidizing attack on the ethylene molecule gives rise to the formation of an intermediate that in the presence of activated ammonia evolves to the final formation of acetonitrile, or in the presence of a second oxygen species to the rupture of the C–C bond with possible formation of formaldehyde, which is easily and quickly transformed to CO.

This hypothesis for the reaction mechanism is speculative, and confirmation will require detailed investigations, but it does explain the nature of the products observed, the similarity between the behaviour of ethane, propane and propene, and the equimolecular formation of acetonitrile and CO from C_3 hydrocarbons. These facts cannot be simply interpreted on the basis of the known mechanisms of selective (amm)oxidation[6,11] and thus suggest the presence of an active site able to bring about a selective electrophilic oxygen attack on the double bond at high temperature, probably analogous to that observed for the unique and very different Ag/Al_2O_3 system using ethylene. The different reaction conditions give rise to a different reaction pattern and nature of final products compared to the silver system. However, these preliminary indications suggest the presence of a similar key step in the mechanism. By a suitable tuning of the properties of Al_2O_3-supported Nb–Sb oxide catalysts it should be possible not only to optimize the synthesis of acetonitrile from ethane, but perhaps also to develop new reactions based on this catalyst and requiring a similar key step, such as the synthesis of acetic acid from ethane.

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