40. The Gas-Phase Ammoxidation of *n*-Hexane

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Abstract

This chapter reports about an investigation on the catalytic gas-phase ammoxidation of *n*-hexane aimed at the production of 1,6-C_6 dinitriles, precursors for the synthesis of hexamethylenediamine. Catalysts tested were those also active and selective in the ammoxidation of propane to acrylonitrile: rutile-type V/Sb and Sn/V/Nb/Sb mixed oxides. Several *N*-containing compounds formed; however, the selectivity to cyano-containing aliphatic linear C_6 compounds was low, due to the relevant contribution of side reactions such as combustion, cracking and formation of heavy compounds.

Introduction

Hexamethylenediamine (HMDA), a monomer for the synthesis of polyamide-6,6, is produced by catalytic hydrogenation of adiponitrile. Three processes, each based on a different reactant, produce the latter commercially. The original Du Pont process, still used in a few plants, starts with adipic acid made from cyclohexane; adipic acid then reacts with ammonia to yield the dinitrile. This process has been replaced in many plants by the catalytic hydrocyanation of butadiene. A third route to adiponitrile is the electrolytic dimerization of acrylonitrile, the latter produced by the ammoxidation of propene.

These processes are used commercially for many years. However, an interest exists for the development of alternative technologies for HMDA production, that may offer advantages with respect to conventional ones, such as: (i) the use of less dangerous reactants, and (ii) a better overall economics, also achieved by the use of highly selective catalytic systems. One possible synthetic pathway is the gas-phase ammoxidation of *n*-hexane to 1,6-C_6 dinitriles, the latter containing either a saturated or an unsaturated aliphatic chain; these dinitriles can be hydrogenated to obtain the diamine.

$C_6H_{14} + 2\ NH_3 + (6+x/2)/2\ O_2 \rightarrow NC\text{-}(C_4H_{8-x})\text{-}CN + (6+x/2)\ H_2O$ (x = 0 to 4)
$NC\text{-}(C_4H_{8-x})\text{-}CN + (4+x/2)\ H_2 \rightarrow NH_2\text{-}(CH_2)_6\text{-}NH_2$ (HMDA)

The catalytic gas-phase ammoxidation of alkanes to aliphatic nitriles has been the object of several investigations in recent years, but the great majority of papers deal with the direct transformation of propane to acrylonitrile, as an alternative to the commercial process of propylene ammoxidation. Two catalytic systems have been proposed in literature for propane ammoxidation: (i) rutile-type metal antimonates, based on V/(Al,W)/Sb/O (1,2) and (ii) multicomponent molybdates (Mo/V/Nb/Te/O) (3). A few papers and patents report about the ammoxidation of C_4 hydrocarbons (butenes, *n*-butane, butadiene) to maleonitrile and fumaronitrile (4,5). The best results were obtained with a catalyst made of TiO_2-supported oxidic active phase containing V, W, Cr and P, and with butadiene as the reactant. With *n*-butane, the highest yield to nitriles was 26%. Some papers deal with the ammoxidation of C_6 hydrocarbons (6,7). In ref. 6, the ammoxidation of *n*-hexane is carried out with a catalyst based on V/P/Sb/O. At 425°C, 40% adiponitrile selectivity and 30% hexanenitrile selectivity were obtained at 12% conversion. In ref. 7, the catalyst described is a Ti/Sb mixed oxide; from cyclohexane, the main products obtained in a pulse reactor were adiponitrile and benzene, with an overall selectivity of more than 90%. An important aspect pointed out by the authors was the strong interaction that develops between the catalyst surface and the nitriles and that favours the occurrence of consecutive reactions and hence the formation of heavy by-products.

In the present chapter, we report about an investigation of the catalytic performance of rutile-type V/Sb and Sn/V/Sb/Nb mixed oxides in the gas-phase ammoxidation of *n*-hexane. These catalysts were chosen because they exhibit intrinsic multifunctional properties; in fact, they possess sites able to perform both the oxidative dehydrogenation of the alkane to yield unsaturated hydrocarbons, and the allylic ammoxidation of the intermediate olefins to the unsaturated nitriles. These steps are those leading to the formation of acrylonitrile in propane ammoxidation. The Sn/V/Sb/(Nb)/O system is one of those giving the best performance in propane ammoxidation under hydrocarbon-rich conditions (8,9).

Experimental

Sn/V/Nb/Sb/O catalysts were prepared with the co-precipitation technique, developed for the synthesis of rutile SnO_2-based systems claimed by Rhodia (8). The preparation involved the dissolution of $SnCl_45H_2O$, $VO(acac)_2$, $SbCl_5$ and $NbCl_5$ in absolute ethanol, and by dropping the solution into a buffered aqueous solution maintained at pH 7. The precipitate obtained was separated from the liquid by filtration. The solid was then dried at 120°C and calcined in air at 700°C for 3 hours. The V/Sb/O catalyst was prepared by means of the "slurry" method that consists in a redox reaction between Sb_2O_3 and NH_4VO_3 in water medium, for 18h at 95°C. The solvent is then evaporated and the solid obtained is dried and then calcined in air at 650°C.

Catalytic tests were performed in a gas-phase continuous-flow reactor. The outlet flow of the reactor was either sampled for the analysis of the gaseous components, or condensed in a dry frozen trap, for the analysis of the solid and liquid products. Two liquid layers formed: an organic layer containing the unconverted *n*-hexane, and an aqueous layer; some products dissolved preferentially in the organic layer, others in the aqueous one. Both layers were analyzed by gas chromatography.

Results and Discussion

Figure 40.1 reports the flammability diagrams for the ternary mixtures: ammonia/oxygen/inert and *n*-hexane/oxygen/inert. The boundary conditions for the catalytic tests were the following:

1. Due to the narrow safe area in the hydrocarbon-lean zone, operation in the *n*-hexane-rich zone was preferred. In the latter case, however, feed compositions having high hydrocarbon concentration had to be avoided, in order to limit the contribution of radical-chain reactions, favoured at high temperature under aerobic conditions. Therefore, operation with a diluted feed was preferred; the ballast used for the reaction was helium, in order to allow evaluation of the amount of N_2 produced by ammonia combustion.
2. Hydrocarbon-rich conditions imply that oxygen is the limiting reactant, due to the high oxygen-to-hydrocarbon stoichiometric ratio in *n*-hexane ammoxidation. Therefore, the conversion of the hydrocarbon is low; this should favour, in principle, the selectivity to products of partial (amm)oxidation instead of that to combustion products.

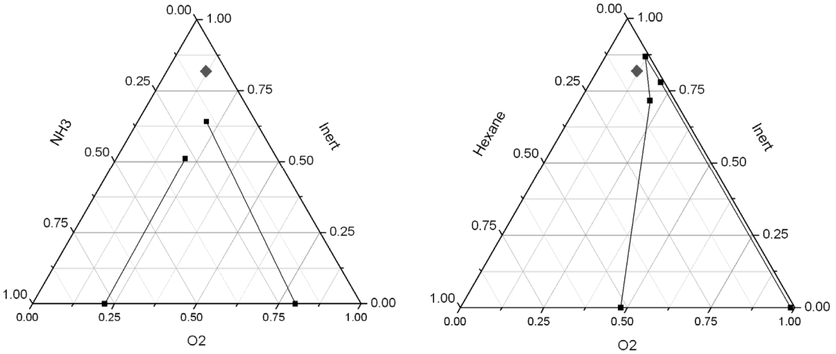

Figure 40.1. Flammability areas for NH_3/O_2/inert and *n*-hexane/O_2/inert mixtures. ♦: Experimental feed composition used for catalytic tests.

The feed composition chosen was: 6 mol% *n*-hexane, 6 mol% ammonia, 12 mol% oxygen and remainder helium, with an overall gas residence time of 2.5 s. Due to the low temperature of *n*-hexane self-ignition (T 234°C), a relevant contribution of homogeneous, radical reactions was expected. Tests made in the absence of catalyst and with the empty reactor, evidenced that at 310°C the conversion of *n*-hexane was 4%, and that of oxygen was 13%. However, already at 330°C the conversion of *n*-hexane and of oxygen were higher than 20 and 30%, respectively. Under these conditions, the main products of the reaction were CO, CO_2 but also a relevant amount of heavy compounds formed downstream the catalytic bed; these compounds led to the blockage of the reactor exit. These problems were in part avoided by minimizing the post-catalyst void fraction in the reactor; the latter was filled with packed quartz-wool, while the void space up-stream the catalytic bed was filled with corundum beads. Under these conditions, the conversion of *n*-hexane in the absence of catalyst was lower than 10% up to 450°C; therefore, this made possible enlarge the temperature zone for catalytic tests, while minimizing the undesired contribution of homogeneous, radical reactions.

Catalysts tested for the reaction of *n*-hexane ammoxidation are reported in Table 40.1. Samples with composition Sn/V/Nb/Sb (atomic ratios between components) equal to x/0.2/1/3 were prepared and characterized. The atomic ratio between V, Nb and Sb was fixed because it corresponds to the optimal one for the active components when these catalysts are used for propane ammoxidation (10).

Table 40.1. Catalysts prepared, and value of specific surface area.

Composition, atomic ratios	Surface area, m^2/g
Sn/V/Nb/Sb 1/0.2/1/3	74
Sn/V/Nb/Sb 3/0.2/1/3	76
Sn/V/Nb/Sb 5/0.2/1/3	82
SnO_2	92
V/Sb 1/1	10

Figure 40.2 shows the X-ray diffraction patterns of Sn/V/Nb/Sb/O catalysts, after calcination at 700°C. All samples showed the reflections typical of the rutile-type compounds, with crystallite size ranging from 7 to 10 nm. There was no relevant effect of the composition on the catalyst surface area. The low crystallinity degree of samples was the reason for the high value of the surface area (reported in Table 40.1), remarkably higher than that typically reported for rutile-type mixed oxides prepared with conventional methodologies like the slurry-redox method. With the latter method, surface area is usually of 10 m^2/g or less. This difference was due to the preparation procedure of our samples, the co-precipitation from the alcoholic medium. This method avoided the segregation of the single metal oxides, and allowed obtaining the rutile mixed oxide by a thermal treatment to be carried out even at temperatures as low as 500°C. Higher catalyst surface areas should allow carrying out the ammoxidation reaction at milder reaction temperatures, and limit the combustion reactions.

In Sn/V/Nb/Sb/O catalysts, different compounds form (10): rutile SnO_2 (also incorporating Sb^{5+}), Sb/Nb mixed oxide and non-stoichiometric rutile-type V/Nb/Sb/O; the latter segregates preferentially at the surface of the catalyst. Tin oxide (cassiterite) provides the matrix for the dispersion of the active components; therefore, a variation of the value of x in Sn/V/Nb/Sb x/0.2/1/3 catalysts implies a change of the ratio between the catalytically inert tin oxide and the components of the active phase. A higher dispersion of the active components should allow minimizing consecutive reactions occurring on both reactants and products, which may be favoured at high concentration of the oxidizing sites.

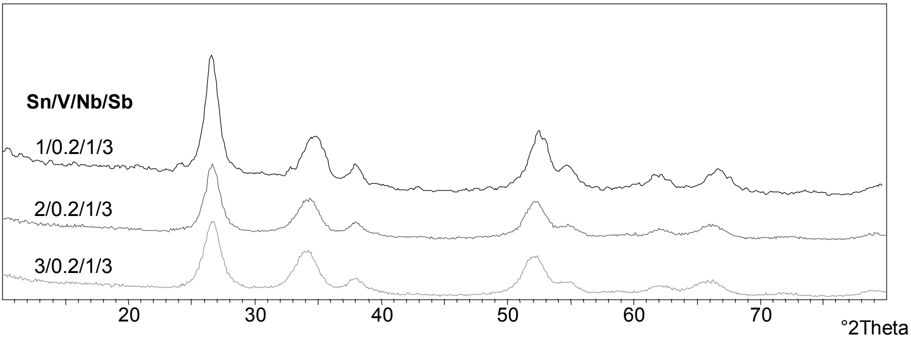

Figure 40.2. X-ray diffraction patterns of Sn/V/Nb/Sb/O catalysts.

The results of reactivity tests performed with catalyst Sn/V/Nb/Sb 1/0.2/1/3 are summarized in Figures 40.3 and 40.4, which report the conversion of reactants and the selectivity to the main products as a function of temperature, respectively. The conversion of *n*-hexane was 20% at 475°C, with a 60% oxygen conversion and 45% ammonia conversion. The reaction yielded many products; besides CO and CO_2, several *N*-containing compounds with 1 to 6 C atoms formed (the overall selectivity to these products is given in Figure 40.4): cyanhydric acid, acetonitrile, acrylonitrile, methacrylonitrile, 2-butenenitrile, isobutyronitrile, butyronitrile, fumaronitrile, maleonitrile, cyclopropanecarbonitrile, 2,4-pentadienenitrile, 2-furancarbonitrile, furandicarbonitrile, pyridine, pyrole, 2-methylpyridine, 3-methylpyridine, benzonitrile, 2-pyridinecarbonitrile, 3-pyridinecarbonitrile and 4-pyridinecarbonitrile. Small amounts of linear aliphatic C_6 nitriles formed: muconodinitrile, hexanenitrile, 2,4-hexadienenitrile and adiponitrile. However, the overall selectivity to these compounds was less than 2%.

Undesired side reactions, i.e., combustion, cracking to light *N*-containing compounds and cyclization of C_6 unsaturated dinitriles, were the reason for the low selectivity to the desired products. The selectivity to C_1-C_5 nitriles increased when the reaction temperature was increased, and that to C_6 nitriles (mainly cyclic compounds) correspondingly decreased. The highest selectivity, amongst nitriles, was to fumaronitrile (17% at 475°C). Another side reaction was the combustion of ammonia; however, the yield to N_2 (also reported in Figure 40.4) decreased when the reaction temperature was increased; at the same time, in fact, the selectivity to *N*-containing compounds became higher. Figure 40.4 also reports the carbon balance, as calculated from the ratio between the overall C atoms found in the products identified, compared to C atoms transformed due to converted *n*-hexane. It is shown that the balance was lower than 50% for reaction temperatures below 400°C, and it increased when the reaction temperature was increased. A carbon balance much lower than 100% indicates that a considerable amount of the formed products has not been analyzed. This was due to the formation of heavy by-products that accumulated in the condenser after the reactor and were not eluted in the GC column.

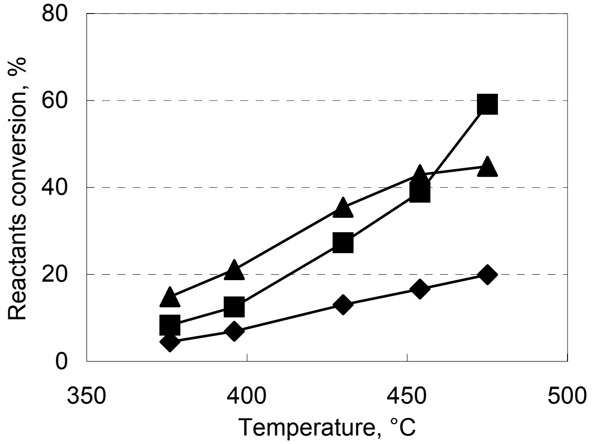

Figure 40.3. Conversion of reactants in *n*-hexane ammoxidation as a function of the reaction temperature. Symbols: conversion of *n*-hexane (◆), ammonia (▲) and oxygen (■). Catalyst Sn/V/Nb/Sb 1/0.2/1/3.

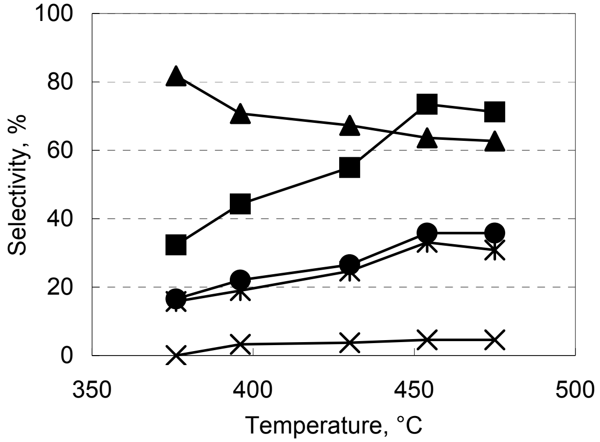

Figure 40.4. Selectivity to products in *n*-hexane ammoxidation as a function of the reaction temperature. Symbols: selectivity to CO (✕), CO_2 (✱), *N*-containing compounds (●, calculated with respect to *n*-hexane converted) and N_2 (▲, calculated with respect to ammonia converted). Carbon balance (■). Catalyst Sn/V/Nb/Sb 1/0.2/1/3.

Figure 40.5 compares the conversion of ammonia and *n*-hexane for catalysts with composition Sn/V/Nb/Sb x/0.2/1/3, while Figure 40.6 reports the overall selectivity to *N*-containing compounds. Surprisingly, the samples containing the greater amount of Sn were the most active. This result was quite unexpected, because tin oxide was catalytically inert when used as one component in catalysts for propane ammoxidation.

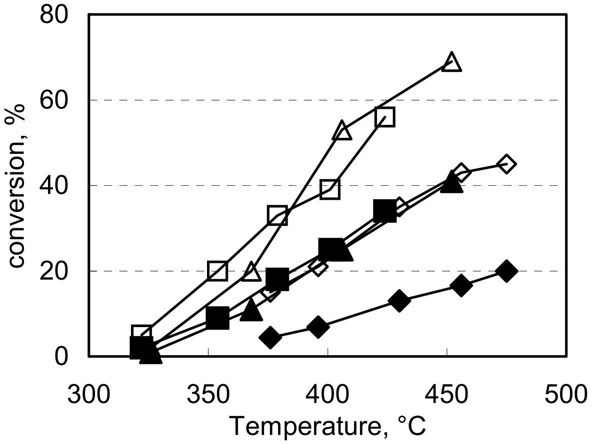

Figure 40.5. Conversion of *n*-hexane (full symbols) and of ammonia (open symbols) as a function of temperature for catalysts with composition Sn/V/Nb/Sb x/0.2/1/3. Symbols: x = 1 (◆◇), 3 (■□) and 5 (▲△).

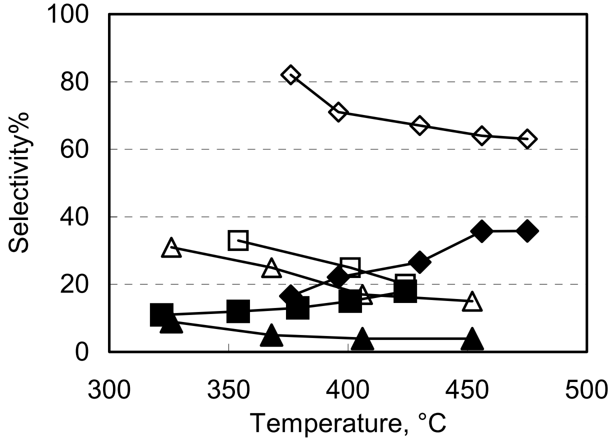

Figure 40.6. Selectivity to *N*-containing products (full symbols, calculated with respect to *n*-hexane converted) and to N_2 (open symbols, calculated with respect to ammonia converted) as a function of temperature for catalysts with composition Sn/V/Nb/Sb x/0.2/1/3. Symbols as in Figure 40.5.

The selectivity to *N*-containing compounds was the lower with catalysts having the greater amount of Sn (x=3 and 5). The yield of products having more than 2 C atoms was very low; in fact the prevailing products were cyanhydric acid and acetonitrile. The main product of the reaction was CO_2, with negligible formation of

CO, while the carbon balance was between 40 and 60% for the catalyst with x=3, and lower than 40% for the catalyst with x=5. On the other hand, the selectivity to N_2, formed by ammonia combustion, was much lower than that obtained with Sn/V/Nb/Sb 1/0.2/1/3. Therefore, in catalysts with the greater amount of Sn, most of N was contained in products that were not detected and that contributed to the relevant loss in carbon balance.

The results indicate that tin oxide plays a direct role in the reaction, addressing the reaction towards the formation of heavy compounds, carbon oxides and cyanhydric acid. This was confirmed by carrying out reactivity tests with the sample made of SnO_2 only; its activity was just the same as that one of samples Sn/V/Nb/Sb x/0.2/1/3 having x=3 and 5. The conversion of ammonia and the selectivity to N_2 were low, and the prevailing products were carbon oxides and heavy compounds. Furthermore, a non-negligible amount of cyanamide formed, that in part oligomerized to form melamine; these compounds, however, were not quantified. Therefore, in the gas-phase ammoxidation of *n*-hexane to linear C_6 dinitriles the main limitation to the selectivity is the concomitant occurrence of several undesired side reactions: (a) The cracking of the reactant and of the unsaturated aliphatics intermediately formed to lighter hydrocarbons. The latter undergo ammoxidation to yield saturated and unsaturated C_1-C_5 nitriles. (b) The combustion of *n*-hexane and of intermediates to CO_2. (c) The combustion of ammonia to N_2, a reaction in competition with the insertion of N to yield *N*-containing compounds. (d) The formation of cyclic C_6 compounds (pyridinecarbonitriles); the latter may occur either by cyclization of unsaturated linear nitriles, or by condensation of lighter nitriles. (e) The formation of heavy compounds and tars.

The reaction mechanism is likely similar to that one commonly accepted for the ammoxidation of propane to acrylonitrile (11). The activation of *n*-hexane may occur via formation of radical species, that either oxidehydrogenate to yield unsaturated C_6 olefins and diolefins, or undergo fragmentation to yield lighter aliphatics. Therefore, the high selectivity to the several C_1-C_5 *N*-containing products obtained is due to the higher reactivity of *n*-hexane as compared to propane, and to the several possible fragmentations of the molecule. In fact, in propane ammoxidation the Sn/V/Nb/Sb/O catalyst yields cyanhydric acid, acetonitrile and acrylonitrile, but the selectivity to acrylonitrile is greater than that to the C_1 and C_2 nitriles. In *n*-hexane ammoxidation, cracking of the C_6 intermediates is quicker than N insertion, and finally the overall selectivity to *N*-containing linear C_6 compounds is lower than the selectivity to lighter compounds.

The catalyst composition has a role in the control of selectivity. The rutile-type V/Sb/(Nb) mixed oxide activates the hydrocarbon and ammonia. However, most of the ammonia is burnt to N_2, rather than being inserted on the hydrocarbons; this likely occurs because the catalyst is not very efficient in the generation of the selective Me=NH species when reaction temperatures lower than 400°C are used (11). In fact, with all catalysts the selectivity to *N*-containing compounds increased when the reaction temperature was increased, and the selectivity to N_2 correspondingly decreased (Figure 40.6). The dilution of the active phase with tin oxide, a component that we supposed to be catalytically inert, decreased the extent of ammonia combustion to nitrogen, but on the other hand it unexpectedly contributed to the conversion of *n*-hexane and to the formation of by-products, such as heavy compounds, cyanamide, cyanhydric acid and CO_2. Therefore, tin oxide is able to activate *n*-hexane, generate radical species and finally favour the fragmentation into lighter compounds. In samples with the greater amount of Sn (x=3 and 5), the low concentration of the active sites able to perform the selective insertion of N led to an enhancement of side reactions occurring at the surface of tin oxide, such as combustion and cracking of the radical intermediates to CO_2 and to light *N*-containing compounds, but also coupling or condensation reactions to yield tars.

In order to confirm the hypothesis made on the role of catalyst components, we carried out the reaction with a rutile-type V/Sb/O catalyst, having V/Sb atomic ratio equal to 1/1 (Table 40.1). This catalyst was prepared with the conventional slurry method, and therefore had a surface area of 10 m^2/g, lower than that obtained with the Sn/V/Nb/Sb/O catalysts prepared with the co-precipitation method. However, despite this difference, with V/Sb/O the conversion of *n*-hexane was similar to that one obtained with Sn/V/Nb/Sb/O. This is shown in Figure 40.7, which reports the conversion of *n*-hexane, the selectivity to CO_2, to *N*-containing compounds and the carbon balance as a function of the reaction temperature.

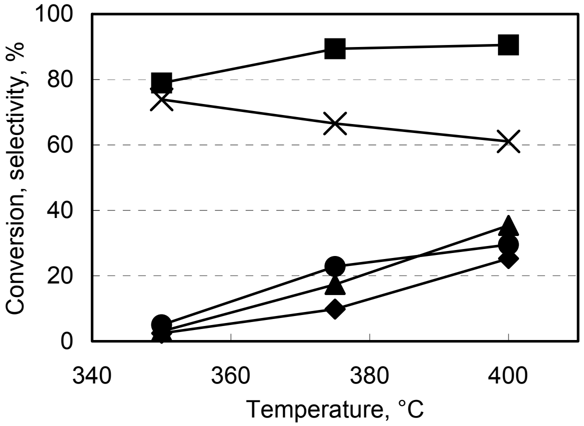

Figure 40.7. Conversion of *n*-hexane (◆) and of ammonia (▲), selectivity to CO + CO_2 (✕), to *N*-containing compounds (●) and carbon balance (■) as a function of the reaction temperature. Catalyst V/Sb 1/1.

The activation energy for *n*-hexane conversion was 37±5 kcal/mole, while it was 17±2 kcal/mole for the Sn/V/Nb/Sb 1/0.2/1/3 catalyst (Figure 40.3). Therefore, with the high-surface-area Sn/V/Nb/Sb/O catalyst, the particle efficiency was largely lower than 1, while this was not the case for the non-porous low-surface-area V/Sb/O. This is likely due to the high intrinsic reactivity of *n*-hexane. For what concerns the selectivity, the main characteristics of the V/Sb/O catalyst were the following (Figure 40.7): (a) a carbon balance close to 80-90%, that indicates the low formation of heavy compounds; (b) a selectivity to CO_2 + CO higher than 70%; and

(c) a relevant degree of ammonia combustion to N_2. The overall selectivity to *N*-containing compounds increased when the reaction temperature was increased. At 350°C, the prevailing *N*-containing compounds were C_6 nitriles and dinitriles. The selectivity to *N*-containing C_4-C_6 products became nil when the reaction temperature was increased, whereas the selectivity to C_1-C_3 nitriles increased. This confirms the hypothesis of an enhanced contribution of cracking reactions and of a higher efficiency in *N*-insertion at temperatures higher than 350°C.

Conclusions

The gas-phase ammoxidation of *n*-hexane to nitriles was investigated using rutile-type Sn/V/Nb/Sb and V/Sb mixed oxide catalysts. Several *N*-containing C_1-C_6 compounds formed; however, the selectivity to cyano-containing aliphatic linear C_6 compounds was low, due to the relevant contribution of side reactions such as combustion, cracking, combustion of ammonia and formation of tars. The ratio between catalyst components influenced the catalytic performance; catalysts having the greater amount of Sn were the least selective, because SnO_2 promoted the formation of CO_2, of light *N*-containing compounds and of heavy compounds.

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