

TPD-TPR-MS Mechanistic Study of the Ammoxidation of 2-Methylpyrazine over Sb-V-Mn-O Catalyst

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Received November 19, 1989; revised February 18, 1991

The setting up of a TPD-TPR-MS apparatus particularly suited to the study of the mechanisms of heterogeneous catalytic reactions is described. The system has been employed for the study of the ammoxidation of 2-methylpyrazine. The information collected showed that all the reactants and products except oxygen adsorb competitively on at least two types of site on the catalyst surface. From sites of the first type (the lower-energy sites) they desorb unaltered, while sites of the second type are higher-energy sites on which the reactants are activated both for the desired reaction to 2-cyanopyrazine and for the decomposition to by-products. Ammonia adsorbs also on a third type of site (very high-energy sites), which are able to activate the molecule for the oxidation to N₂ and NO_x. Oxygen does not compete in adsorption with any of the other species. Very likely it dissolves in the solid, rapidly diffusing through the bulk and is involved in the reaction through a Mars-van Krevelen mechanism. A Rideal-Eley type of mechanism, with either oxygen or ammonia coming from the gas phase, seems not to be supported by the present results. © 1991 Academic Press, Inc.

INTRODUCTION

The exploitation of the temperature-programmed desorption or temperature-programmed reaction techniques (TPD-TPR) has enjoyed a considerable development since the 1960's, after the fundamental work by Amenomiya and Cvetanovic (1, 2), who developed the theoretical basis of the method. By coupling this technique with the highly sensitive quadrupolar mass spectrometric (MS) detector, a very versatile tool for the study of reacting catalytic systems is obtained. There have been a number of reports since 1980 on the application of the TPD-TPR-MS technique (3-8).

In some previous papers (9-15) we reported on a simple, two-step catalytic route for the preparation of 2-amidopyrazine (AP), a well-known antitubercular drug, starting from the cyclization of ethylenediamine (ED) and propyleneglycol (PG) to 2-methylpyrazine (MP), followed by ammoxidation

of the latter by air and ammonia to 2-cyanopyrazine (CP), which spontaneously hydrolyzes in aq. ammonia to AP. In the present paper we report on the application of the TPD-TPR-MS technique to the study of the mechanism of the second step of this process, namely the catalytic ammoxidation of MP to CP.

EXPERIMENTAL

Apparatus. The apparatus consists of four sections: (i) metering and mixing of feeding gases, (ii) sorption and reaction, (iii) temperature control, and (iv) computer-aided analysis and monitoring of the effluent gas.

A general sketch is shown in Fig. 1. The flow rate of the carrier gas (SIAD ultrapure grade helium, ≥ 99.99995 vol%) is regulated by a Brooks mass flow controller, equipped with on-line filter, flow sensor, control valve, and preceded by a shut-off valve. Periodical calibration by means of a microburette soap-bubble flow meter in series showed a deviation from the set point never larger than ±0.1%. Pulses of gaseous re-

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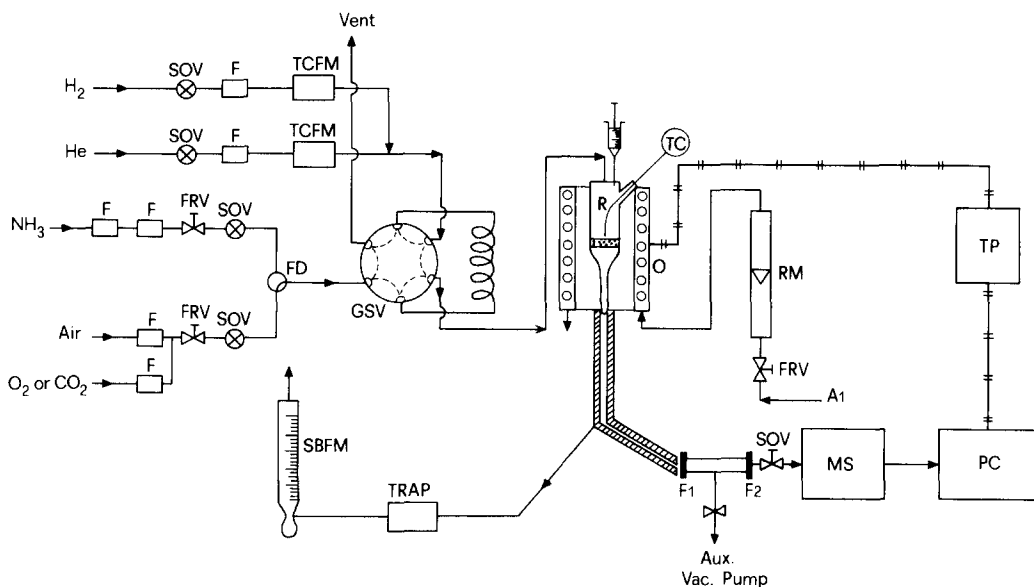


FIG. 1. Sketch of the experimental set-up. SOV, shut-off valve; F, filter; TCFM, thermal-conductivity flow-meter; FRV, flow-regulating valve; GSV, gas-sampling valve; TC, thermocouple; R, reactor; O, furnace; RM, rotameter; TP, temperature programmer; MS, mass spectrometer; PC, computerized driving unit; SBFM, soap-bubble flow-meter; F1, F2, interchangeable laser-pierced Mo sheets.

agents (NH_3 , air, CO_2 , or O_2) are made through a six-way gas sampling valve, equipped with dosing capillary ranging in volume from 0.075 to 1.00 cm^3 . Pulses of liquid or solid reagents are injected just before the catalyst bed, through a rubber septum and by means of a microsyringe or of a solid injector, respectively.

The reactor is a 7-mm inner diameter pyrex glass tube, in which the catalyst is placed on a small plug of quartz wool supported on a fritted disk. Particular care was given to minimizing the dead volume after the catalyst bed, by reducing the internal diameter of the reactor to 1.75 mm and by connecting the latter to the detector inlet by means of 2×1 -mm diameter stainless-steel tubing of as short a length as possible. As a result, with the usual carrier gas flow rate of 20 cm^3/min , the time required for an inert gas dose to pass from the injection port to the detector was ca. 1 s. To avoid condensation of liquid or solids, the reactor to detector connection and the MS prechamber are

maintained at ca. 170°C by means of a hot foil.

The reactor is heated by means of an electric furnace, equipped with a stainless-steel tubular coil, through which a continuous flow of cooling air is passed at the desired flow rate, controlled by a manual regulating valve and monitored by a rotameter. This ensures a good temperature control, both in isothermal and in programmed-temperature mode. The temperature is controlled by an Inconel-sheathed thermocouple (0.25 mm external diameter of the sheath), directly dipped in the catalyst bed and connected to a Eurotherm PIDD temperature-programmer, equipped with power unit. An auxiliary 0 to 12-V output permits us to monitor the temperature also by means of the computer governing the MS detector.

The gas coming from the reactor is analyzed and monitored by means of a UTI mod. 100 C quadrupolar mass spectrometer, connected to the gas line through a prechamber, in which an auxiliary vacuum pump

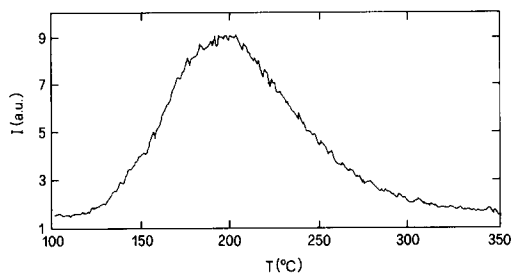


FIG. 2. Typical desorption curve of MP in sorption-desorption tests of pure species.

maintains a residual pressure of ca. 0.3 Pa. The flow of gas entering the spectrometer chamber is regulated by means of two very small holes (e.g., 30 and 50 μm , respectively) laser-pierced through interchangeable molybdenum sheets, placed at the inlet of the prechamber and of the chamber, respectively. The turbomolecular-mechanical-pump vacuum system maintains a residual pressure of the order of 10^{-4} Pa in the MS chamber. The latter can be isolated for bake-out cleaning purposes by means of an all-metal Nupro shut-off valve placed at the chamber inlet. The vacuum in the various sections of the apparatus is monitored by means of a Granville-Phillips multiport instrument.

The analytical system is governed by a PC, interfaced both with the MS control unit and with the temperature-programmer through proper card boards and equipped with high-definition color monitor. A set of different software programs and subroutines permits us to collect, store, and process the analytical data in many different ways.

Catalyst. The catalyst was prepared and characterized during the previous screening and optimization work (9-11). The composition, the main physico-chemical characteristics, and some typical performance data are summarized in Table 1.

Reagents. Liquid and solid reagents, MP, CP, and pyrazine (P), were pro analysi Fluka, C. Erba, or Merck products. Gaseous reagents, ammonia (SIAD, Transistor

grade), air, oxygen, and CO_2 (SAPIO or SIAD, superpure grade) were ≥ 99.999 vol% pure. All the reactants were employed as supplied.

Procedure. Different procedures have been followed for the collection of data, depending on the information desired. Such procedures have been defined after proper sets of preliminary experiments aimed at defining the correct range of values of the experimental parameters within which reproducible and reliable data could be collected in the various cases, e.g., in temperature-programmed or in isothermal mode. Together with the usual parameters (catalyst weight, temperature, carrier gas flow rate, number, and size of reactant pulses), we considered some special ones, such as the temperature of the connection between the reactor outlet and analytical system, fresh catalyst pretreatment conditions and the procedure of catalyst cleaning after the run.

The first group of experiments was carried out under subsaturation conditions. A quick calculation, based on the physical properties of the catalyst, showed that when injecting 0.1 μl of the liquid reactant (MP) or 0.1 ml of the gaseous reactants on the usual 100- to 200-mg catalyst charge, no more than a few percent of the surface sites can be covered, even if the whole amount of the species injected were to be adsorbed. Hence, in these tests, no more than 0.3 μl of liquid or 0.2 ml of gaseous reagent, respectively, was injected in each run.

Catalyst cleaning-up procedure. As revealed by our previous work (9-11) the active phase of the catalyst is $\alpha\text{-Sb}_2\text{O}_4$, the V and Mn promoters being added only to improve both selectivity and catalyst life. This is a metastable phase, tending to the thermodynamically stable, but catalytically inactive, Sb_2O_3 (16). In the absence of molecular oxygen in the gas contacting the solid, the transformation is sufficiently slow only at $T < 550^\circ\text{C}$, becoming quite rapid at $T > 800^\circ\text{C}$. As a consequence, not only could a maximum temperature of 550°C not be exceeded, but also the time of maintaining

TABLE I

Principal Characteristics of the Sb-V-Mn-O Catalyst Employed (see Refs. (9, 11))

Sb/V/Mn (atomic ratio)	21.6/2.5/1		
BET surface area (m ² /g)	5.2		
Pore volume (cm ³ /g)	0.12		
	$pK_a = \leq -1.5$	≤ 1.5	≤ 6.8
Surface acidity ($\mu\text{eq/g}$)	45	53	172
Particle size (mm)	0.25–0.18		
Optimal reaction temperature range (°C)	350–400		
	Excess of steam		Absence of steam
Conversion (mol% of fed MP) ^a	87.5		83.7
Selectivity (mol% of reacted MP transformed into CP)	62.9		13.8

^a Conversion and selectivity data refer to steady-state, continuous, tubular reactor runs, under optimized reaction conditions.

the catalyst at high temperature had to be kept as short as possible. The standard cleaning-up procedure adopted, ensuring the best compromise, was a TPD ramp (20°C/min) up to 550°C, followed by holding for 15 min at this temperature. However, after a considerable number of runs or after heavy contamination, some organic residue remained adsorbed, leading to poorly reproducible data. In such a case a fresh catalyst sample was charged.

RESULTS AND DISCUSSION

Sorption-desorption of pure species. The sorptive properties of the various reactants and products (MP, P, CP, NH₃, O₂, and CO₂) have been tested through a series of runs in which the pure components were adsorbed during an initial 100°C isotherm and then desorbed by means of a TPD ramp, up to a final 500°C isotherm. Before starting the ramp, a sufficient time (usually 30–60 min) was allowed to elapse, to remove from the system the injected, but unadsorbed or very weakly adsorbed reactant. The desorption was monitored through the amu signal corresponding to the parent peak of the various species. An example is shown in Fig. 2. All the species, except O₂, showed a desorption spectrum characterized by one or more maxima. The

temperature T_{max} of the various spectra and the experimental conditions relative to these runs are summarized in Table 2.

Reaction of adsorbed species. The following series of runs was aimed at determining the tendency of the adsorbed species to react or to decompose. The experimental conditions were: reoxidation of the catalyst by means of O₂ pulses at 550°C, cooling and injection (e.g., 0.35 μl of MP) during the initial isotherm (100°C), followed by the usual isothermal removal of the excess (30–60 min) and by the 20°C/min ramp up to a higher-level (550°C) final isotherm (20 min). The most interesting results are shown in Fig. 3a: after the injection of MP, a decomposition of this reactant can be noted, with formation of CO₂ and of P, the latter appearing at higher temperature ($T_{\text{max}} \approx 370^\circ\text{C}$), with respect to the usual desorption of preadsorbed pure P (Table 2). A similar behavior is noted after the injection of CP (Fig. 3b): the latter appears at higher temperature ($T_{\text{max}} \approx 340^\circ\text{C}$) with respect to the second desorption peak ($T_{\text{max}} \approx 270^\circ\text{C}$) observed in the previous experiments (Table 2). Furthermore, if the injection of MP is repeated without reoxidation of the catalyst, no formation of P is observed (Fig. 3c).

These results suggest that at least two dif-

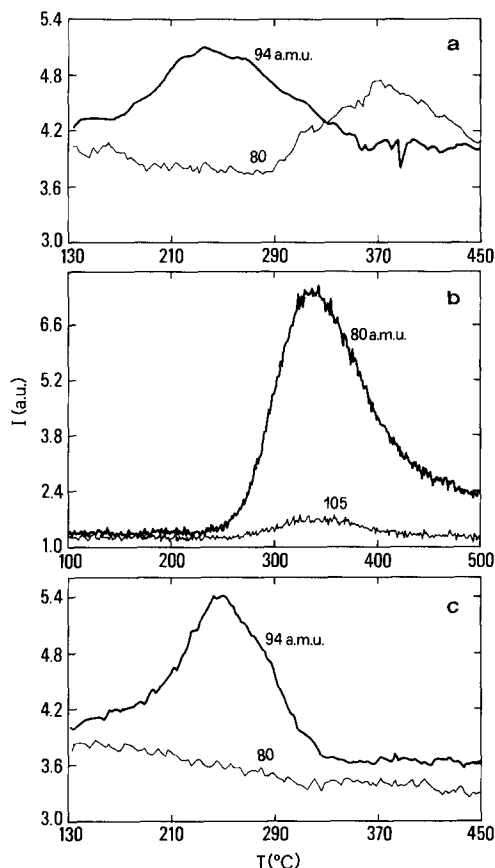


FIG. 3. (a) Desorption curves of MP (amu 94) and P (amu 80), the latter forming by decomposition of MP. (b) Desorption curves of CP (amu 105) and P (amu 80), the latter forming by decomposition of CP. (c) Desorption curve of MP in the absence of catalyst reoxidation.

ferent types of surface site are involved in the sorption–reaction of MP. The situation is similar to that reported for the ammoxidation of 3-picoline over pure V_2O_5 (5), where it was noted that the heterocyclic species can adsorb in two different ways, either through the N atom (on low-energy sites) or through the methyl group (on high-energy sites). Another possible interpretation could refer to the presence of different amounts of oxygen species surrounding the site, according to the various treatments. This would confer a different behavior on the oxygen-poor sites, with respect to the oxy-

gen-rich ones. However, the different behavior of the site, due either to the different concentration of neighboring oxygens, or to the different nature of the site, reveals itself through a different energy of interaction with the adsorbing species. Hence, both the interpretations lead to the same practical result. In our case, the MP adsorbed through the N atom desorbs unchanged, due to the low-energy change involved, insufficient for activating the molecule. Only the fraction of MP adsorbed on high-energy sites is activated for the oxidative degradation to P (and CO_x), through the reaction with oxygen. The latter very likely does not adsorb on the catalyst, but rather “dissolves” in it, since no desorption peaks were ever observed (Table 2), the amu signals of such a species remaining unaltered during all the TPD experiments. The amount of O_2 so available is quite low and it must be resupplied, e.g., by means of air pulses, after each experiment. This hypothesis is confirmed by the trend of the CO_2 signal (amu = 44) at the end of the runs, recorded in the presence (Fig. 4a) or in the absence (Fig. 4b) of catalyst reoxidation. In the latter case the signal returns to the baseline after the peak, while in the former a slow formation of CO_2 may be noted, indicating that some oxygen is still present in the catalytic system, so that the “combustion” of organic fragments can continue.

TABLE 2
Sorption–Desorption of Pure Species^a

Substance	T_{max} (°C)
MP	200
P	200
CP	170 and 270
NH_3	200, 260 and >500
CO_2	390 and >500
O_2	—

^a Catalyst weight = 200 mg, carrier gas flow rate₃ = 20 cm³/min. Pulse volume: liquids = 0.35 μ l, gases = 0.075 cm³, solid (P) = less than 1 mg.

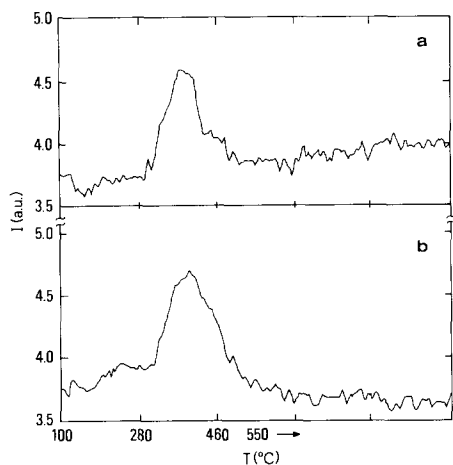


FIG. 4. Desorption curves of CO_2 : (a) in the presence, (b) in the absence of catalyst reoxidation.

Competition of the reactants in adsorption. The competition of the three reactants in adsorption on the catalyst surface has been studied by preadsorbing MP at 100°C as usual, followed by a TPD ramp ($20^\circ\text{C}/\text{min}$) up to 500°C . During the desorption of MP a pulse of air or of NH_3 was injected, while monitoring the behavior of the most interesting amu signals. The results indicate that ammonia competes very strongly with MP while oxygen does not compete at all. Indeed, the injection of NH_3 during desorption of MP (Fig. 5a) causes a neat desorption peak on top of the desorption curve of the latter, while the injection of air leaves the curve completely unperturbed (Fig. 5b).

The analysis of the possible competition in adsorption has been extended also to the whole group of principal products. The runs were carried out by presaturating the catalyst with a given species, followed by the usual TPD ramp, during which pulses of another species were injected as previously described. A substantial modification of the form of the TPD spectrum of the desorbing first species indicates a competition of the second one for the same type of surface site. The set of runs so carried out is summarized in Table 3. The following results were obtained. (i) Ammonia competes with all of the

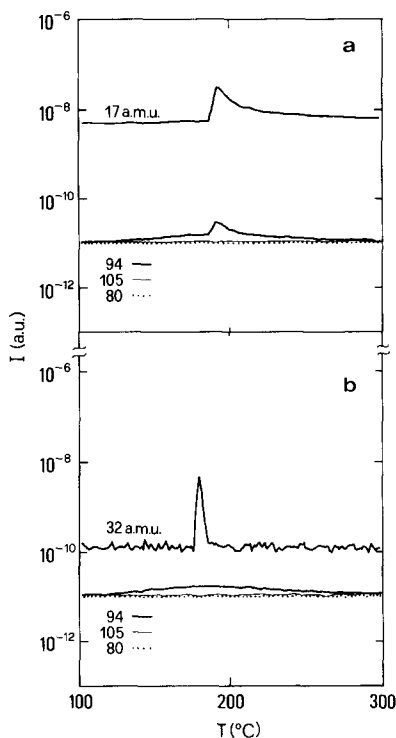


FIG. 5. (a) Pulse of NH_3 (amu = 17) during desorption of MP (amu = 94). (b) Pulse of air (oxygen, amu = 32) during desorption of MP.

preadsorbed species, substituting them both on low- and high-energy sites. (ii) Oxygen does not compete with any species and apparently it seems not to be adsorbing. This suggests that it takes part in the reaction through a Mars-van Krevelen (17) mechanism. (iii) CO_2 pulses do not remove any of

TABLE 3
Competition Tests

Desorbing species	Injected species
MP, P, CP	NH_3
MP, P, CP	O_2
MP, P, CP	CO_2
MP, P, CO_2	NH_3
CO_2	NH_3
MP, P	CP
CP	MP

the organic species at any temperature. (iv) CO_2 is removed by NH_3 only at $T \geq 400^\circ\text{C}$. This indicates that CO_2 adsorbs on different sites, with respect to organic species. (v) All the pyrazinic species (MP, P, and CP) compete for the same type of sites.

Pulses of NH_3 and O_2 under isothermal conditions (500°C). The strong affinity of ammonia for the catalyst was confirmed by a series of runs under isothermal conditions. At any temperature, up to 550°C , ammonia pulses can remove from the catalyst surface not only the relatively weakly bound organic fragments, but also the very strongly bound CO_2 . Hence a special cleaning-up procedure of heavily contaminated catalyst could be envisaged, consisting of injecting a series of NH_3 pulses at 550°C , until the signals corresponding to the contaminating species are no more perturbed by the injection (Fig. 6a). This behavior indicates that ammonia adsorbs on many different types of site. Besides the low-energy ones ($T_{\text{max}} = 210^\circ\text{C}$) from which it desorbs unaltered, it competes with the organic species for adsorption on the high-energy sites, promoting the desired ammoxidation reaction, accompanied by oxidative decomposition of reagents and products. Furthermore, it competes with CO_2 on even stronger adsorption sites.

A further isothermal (500°C) experiment consisting of injecting two NH_3 (0.075 cm^3) pulses, followed by three pure oxygen pulses of the same volume, was carried out on the catalyst just at the end of a standard TPD run (with MP). The result is shown in Fig. 6b. It may be observed that after the injection of NH_3 , a considerable amount of CO_2 (amu = 44) appears, accompanied by water (amu = 18). The amu = 28 signal corresponds to the principal peak of both N_2 and CO, so that one cannot establish which species is evolving on the basis of this signal alone. However, it may be considered that the amu = 12 signal is characteristic of CO_x species and does not correspond to any fragment coming from NH_3 or N_2 , while the amu = 14 signal is characteristic of the latter species and does not correspond to any frag-

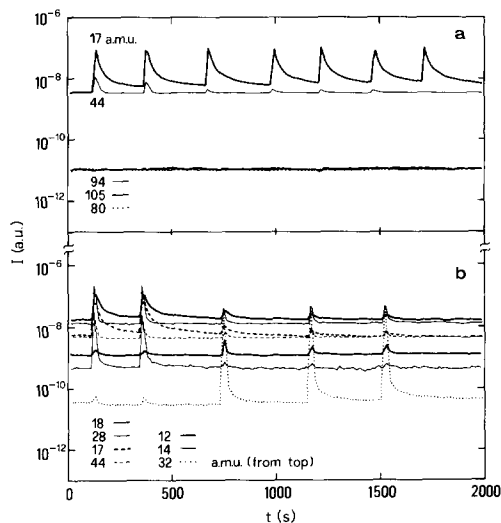


FIG. 6. (a) Example of MS monitoring during the "special" cleaning-up procedure of the catalyst surface. NH_3 pulses of 0.075 cm^3 (amu = 17) at 550°C remove all contaminants, including CO_2 (amu = 44). Note that six more pulses are required to remove the residual CO_2 , after the signals of the heterocyclic species (amu 80, 94, and 105) have become completely flat. (b) Two 0.075 cm^3 pulses of NH_3 (amu = 17, not reported for clarity) under isothermal conditions (500°C), followed by three O_2 pulses (amu = 32). CO_2 desorption (amu = 44) and ammonia oxidation to N_2 (amu = 28 and 14) can be observed when injecting NH_3 . O_2 pulses favor oxidation of organic fragments, with formation of CO_2 and CO (amu = 28 and 12).

ment coming from the former ones. As a consequence, during the first series of pulses the trend of the whole group of signals clearly indicates that the injection of NH_3 is accompanied mainly by the oxidation of the latter to N_2 (strong peaks of amu = 28 and 14 signals) and water (amu = 18). This oxidation is likely to be preceded by a dissociative adsorption of NH_3 , with formation of strongly adsorbed species of the type $\text{NH}=\sigma_2$, σ being a catalyst surface site. From these sites ammonia can desorb no more, the adsorbed species being readily oxidized to N_2 (and H_2O) by the oxygen present in the catalyst.

During the second series of pulses, the relatively large amount of oxygen particularly favors the oxidation of organic frag-

ments still present on the catalyst, with formation of CO (strong amu = 28 and 12 signals) and CO₂, besides water.

TPR runs. The ammoxidation process is carried out industrially in the presence of a large excess of steam, and under steady conditions. However, such conditions could not be reproduced in the present work, due to the intrinsically unsteady nature of the pulse method. Hence, we looked for a satisfactory set of different experimental conditions, ensuring a reasonable formation of the desired product in the absence of steam. Three sets of TPR runs (20°C/min up to 500°C) were carried out as usual for this purpose, after (a) preadsorption of NH₃, followed by injection of MP, (b) preadsorption of MP, followed by injection of NH₃, and (c) simultaneous injection of MP and NH₃. Note that oxygen was not injected, since a previous regeneration of the catalyst with pure oxygen was always carried out, leaving in or on it a sufficient amount of this species. The initial preadsorption–injection isotherms were carried out at 100, 150, and 200°C.

During the initial isotherm at 100°C of the (a) series some NH₃ was observed to desorb (Fig. 7a) with every MP injection, confirming the competition of the two species for the same type of sites (probably the low-energy ones). Very small but increasing amounts of CP were desorbed (Figs. 7a and 7b) with every injection of MP starting from the second one, indicating that the product forms since the first injection, remaining adsorbed and being removed only after a further amount is formed and removed by the competitive adsorption of the reagent. Furthermore, a considerable amount of P (amu = 80) accompanies every MP injection. During the following TPR ramp no CP was noted to desorb, while the desorption of P was clearly evident. This confirms that under these conditions, CP is quite labile and the reaction probably proceeds quickly to P, as confirmed by the runs at 150 and 200°C, during which the CP signal was completely absent.

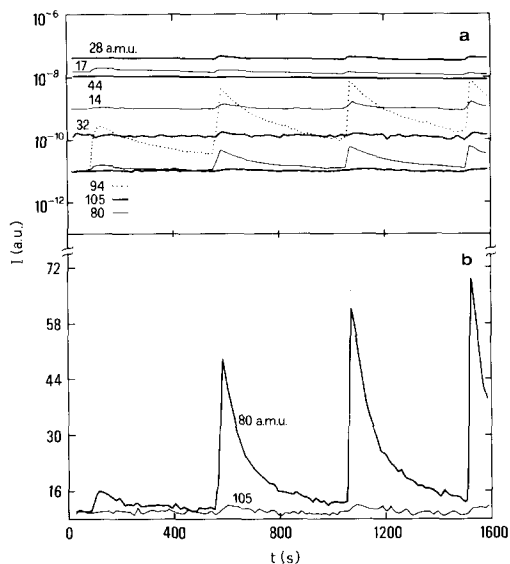


FIG. 7. (a) Initial 100°C isothermal spectra. Effect of MP pulses (amu = 94) after NH₃ preadsorption. (b) Enlargement of the amu = 80 (P) and 105 (CP) signals of Fig. 7a.

The (b) series of runs have been carried out as mentioned, by preadsorbing MP (three 1 μl injection) followed by five 0.075-cm³ NH₃ pulses. The initial isotherms were at 100 or 150°C. During the subsequent TPD ramp up to 500°C, no CP signal was ever observed, while small amounts of P and MP desorbed during the TPD ramp following the 150°C initial isotherm. It was then decided to increase the amount of preadsorbed ammonia, by injecting 1 cm³ pulses, but no CP could be detected in any case during the TPD run. These results tend to exclude, for the present process, a Rideal–Eley type of mechanism between adsorbed MP and the ammonia coming from the gas phase, as suggested for the similar ammoxidation of the 3-picoline (5).

The (c) series of runs, carried out under isothermal conditions by simultaneously injecting both reactants on the freshly regenerated catalyst, was performed by repeating the pulses three times during each run. Every pulse consisted of 1 μl of MP and two 0.075 cm³ or 1 cm³ of gaseous NH₃. After the third pulse a TPD ramp up to a final

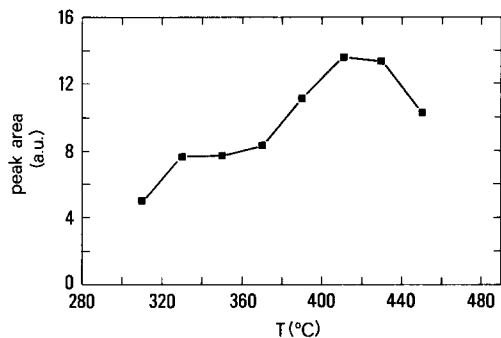


FIG. 8. CP peak area after simultaneous injection of MP and NH_3 vs temperature of the initial isotherm.

500°C isotherm followed and some final NH_3 pulses were then injected at this temperature.

Eight different values of temperature were chosen for the initial isotherm, ranging from 310 to 450°C in 20°C steps. The amount of CP formed has been expressed in terms of the peak area of the $\text{amu} = 105$ signal. By expressing the catalyst productivity as the sum of the peak areas of CP relative to the three injections, one may note an increase up to 410°C, followed by a decrease (Fig. 8). This value of temperature is slightly higher than the optimal value (370°C) found in the presence of steam and under steady conditions. Furthermore, the amount of CP formed after each injection is practically constant for $T \leq 370^\circ\text{C}$, but decreases considerably with the number of pulses for $T > 370^\circ\text{C}$ (Fig. 9), confirming a quicker depletion of oxygen in the catalyst at higher temperatures. This is confirmed also by the runs carried out by injecting larger amounts of NH_3 , leading to larger formation of CP only at lower temperatures (Fig. 10). The formation of the aldehyde (in the present case 2-formyl-pyrazine $\text{amu} = 108$), which is the principal product in the absence of NH_3 , as observed also by others (18) for similar reactions, has been noted in only a few cases and only in very small traces, thus confirming that under the present reaction conditions this species can hardly form or quickly decomposes, presumably to $\text{P} + \text{CO}_x$.

NH_3 oxidation at high temperature. As previously mentioned, the ammonia ad-

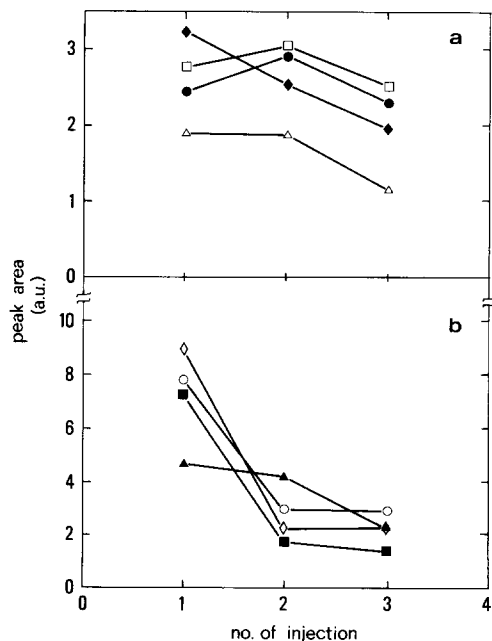


FIG. 9. CP peak area vs No. of subsequent simultaneous injections of MP and NH_3 at different temperature values of the initial isotherm. (Δ) 310, (\bullet) 330, (\blacklozenge) 350, (\square) 370, (\blacktriangle) 390, (\circ) 410, (\diamond) 430, (\blacksquare) 450°C.

sorbed on the highest-energy sites of the catalyst is rapidly oxidized. To obtain more information on this reaction, some runs were carried out by injecting pulses of pure NH_3 on the freshly regenerated catalyst, kept in isothermal conditions at 500°C. It was observed that, besides N_2 ($\text{amu} = 28$), the oxidation leads also to NO_x species, as

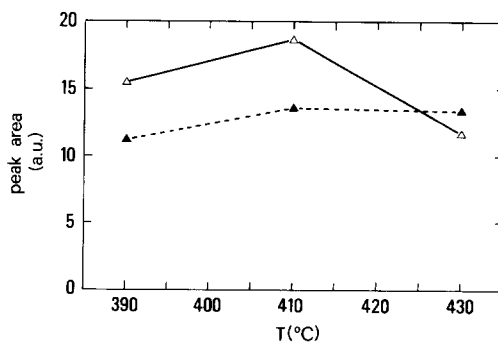


FIG. 10. CP peak area vs temperature value of the initial isotherm for different amounts of injected ammonia. (\blacktriangle) Two 0.075 cm^3 pulses, (\triangle) one 1.0 cm^3 pulse.

revealed by the $\text{amu} = 30$ signal. Further injections of pure O_2 followed by new injections of NH_3 and so on confirmed this mechanism, suggested also by others (19) for a similar process.

CONCLUSIONS

The present experimental set-up proved to be versatile and wholly satisfactory for the study of heterogeneous catalytic reactions, permitting easy collection of much mechanistic information. As for the present ammoxidation process, the principal conclusions one can draw can be summarized as follows.

(i) Reactants and products (MP, NH_3 , CP, P) usually adsorb on at least two types of site. Only from the low-energy sites can they desorb unaltered, with $T_{\text{max}} = 170\text{--}200^\circ\text{C}$. Higher-energy sites ($T_{\text{max}} \cong 270^\circ\text{C}$) are able to activate the reactants both for the desired reaction and for the decomposition of MP and CP to P and lighter products.

(ii) A competition exists for adsorption of all the species on both these types of site.

(iii) In the case of NH_3 , a third, very high-energy type of site ($T_{\text{max}} \geq 500^\circ\text{C}$) activates the molecule for the oxidation to $\text{N}_2 + \text{NO}_x$.

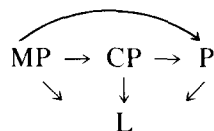
(iv) Oxygen does not compete with other species in adsorption. It is probably involved in the reaction through a Mars-van Krevelen mechanism, by diffusing into the catalyst bulk and reoxidizing the surface active sites as they are reduced by the reaction.

(v) A Rideal-Eley mechanism between adsorbed MP and weakly adsorbed or gaseous NH_3 , as proposed for the ammoxidation of 3-picoline (5), seems not to be supported by the present results.

(vi) MP probably adsorbs on the lower-energy sites through the N atom of the heterocyclic ring. On higher-energy sites it adsorbs through dissociation of the methyl group, with abstraction of one H atom, involving a second, adjacent site. This second mode of adsorption seems to be the one

through which the principal reaction takes place, as proposed for many similar reactions (20-22).

(vii) The simplified reaction scheme previously proposed (15) is still generally acceptable for practical purposes, provided the additional direct decomposition reaction of MP to P is added to the previous ones. The corrected simplified scheme can then be drawn as



L being the decomposition products unrecognizable as pyrazinic species and probably consisting of light fragments forming after cleavage of the pyrazinic ring.

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