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The HDN Reaction Mechanisms of Cyclic Amines on MoO_3/Al_2O_3 Catalyst under Normal H_2 Pressure

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Reactions of cyclic amines (principally 2-6-lutidine and 2-6-lupetidine) have been investigated under normal pressure of H_2 on a MoO_3/Al_2O_3 catalyst. The analysis of the different hydrocarbons and amines formed suggests two forms of adsorption, one "vertical" by the nitrogen doublet and one "horizontal" by the π-electrons of the ring. In addition, the existence of a site of reaction containing two metal atoms more or less reduced is proposed. The formation by hydrodenitrogenation of a large amount of cyclic hydrocarbons, including aromatics such as toluene, is reported for the first time.

INTRODUCTION

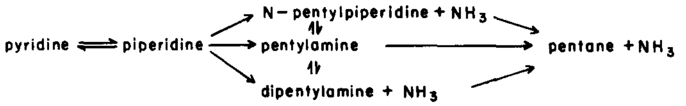
Because of its importance in the refining process of the heavy oil fraction, the hydrodenitrogenation (HDN) of aromatic or cyclic amines has been studied by several authors. Most of the industrial research has been carried out in order to find new catalysts or to improve the yield of the reaction using model compounds often diluted in liquid hydrocarbons. Supported molybdenum or tungsten oxides or sulfides on alumina or silica are generally used with the addition of a group VIII transition metal (*1–6*). New catalysts containing other oxides and ultrastable zeolites have recently been patented by Kittrell (*7*).

McIlvried (*8*), studying the kinetics of pyridine HDN on Ni–Co–MoO_3/Al_2O_3, proposed the general scheme:

$$\text{pyridine} \xrightarrow{H_2} \text{piperidine} \xrightarrow{\text{rds}} \text{pentylamine} \rightarrow \text{pentane} + NH_3$$

(rds = rate-determining step).

Sonnemans *et al.* (*9, 10*), in a study of the same reaction, proposed a more complicated scheme where the disproportionation reaction is the key of the system:



Most of these studies have been made at high pressure of H_2 (generally 60 atm) and surprisingly have totally ignored the initial distribution in the different hydrocarbons formed. In addition, most of the proposed mechanisms ignore the structures of the adsorbed intermediates (*11*). We believe that a study in which amines of different structures are used under normal hydrogen pressure could be very informative for the determination of mechanism. In addition, we also believe that supported catalysts derived from organometallic complexes could be very efficient for the HDN reaction.

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EXPERIMENTAL

(*1*) *Materials.* Amines from Aldrich or Fluka have been used directly after checking their purity by GLC (>99.5%).

(*2*) *Catalyst.* A first catalyst, 12% by weight MoO_3/Al_2O_3, was prepared by impregnation of alumina (Ketjen 217 m^2/g; pore volume, 0.62 cm^3/g) with an ethanolic solution of molybdenyl acetylacetonate, calcination in air at 550°C for 2 h, and reduction *in situ* by hydrogen at 390°C for 24 h (specific surface area, 185 m^2/g).

(*3*) *Apparatus and procedure.* The differential reactor (isobaric and isothermal conditions) has been described elsewhere (*12*). Two calibrated catharometers were inserted in the flow line before and after the reactor in order to estimate the amounts of material left on the catalyst (Fig. 1). In each run, a small amount of the amine (~ 10 μl) was passed over the catalyst (500 or 200 mg) at a constant pressure (5–10 Torr) in a flow of hydrogen (1 atm, 15 ml/min → 170 ml/min). The reaction mixture was analysed by chromatography over a Carbowax 20M, KOH 5% column and a SE 30 silicone column. The Carbowax column allows the separation of the different amines and the aromatic hydrocarbons from the other hydrocarbons (except NH_3 which is eluted together with the various linear and cyclic C_7 hydrocarbons when using a catharometer detector). The SE 30 column allows the separation of the different hydrocarbons formed during the reaction. The toluene, cleanly separated from the other products on both columns, is used to link the two analyses. The different hydrocarbons formed have been identified by mass spectrometry after the chromatographic separation.

RESULTS

In Table 1 are reported the reactions of 2-6-lutidine (2-6-dimethylpyridine). All the runs were made successively in about 3 months on the same catalyst without any treatment or activation except keeping it permanently under a flow of hydrogen. For a fresh catalyst (or one kept under H_2 for a long time >12 h) the first reaction is *always* accompanied by a strong adsorption of reactants on the catalyst (Fig. 2). At low temperature (<275°C) the adsorption is strong even after many successive runs (E14).

The first four reactions (E1–E4) were made at different flow rates of H_2 at 390°C. The formation of the corresponding saturated amine (2-6-lupetidine or 2-6-dimethylpiperidine) diminished quickly only to come back at very low temperature (E14).

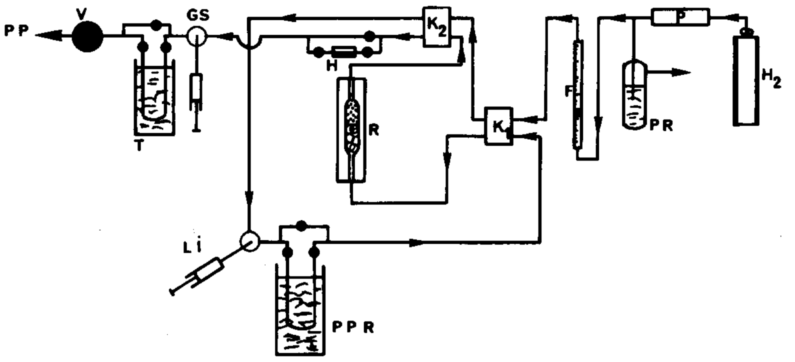


FIG. 1. Reaction apparatus. H_2, Hydrogen cylinder; P, purifier; PR, pressure regulator; F, flowmeter; K_1, K_2, catharometer; Li, liquid injector; PPR, partial-pressure regulator; R, reactor; H, hydrogenator; GS, gas sampler; T, trap in liquid N_2; V, needle valve; PP, primary pump; ●, Teflon valve. From K_1 inlet to V, the all-glass system is maintained at 150°C except in PPR and T.

TABLE 1

Reaction of 2-6-Lutidine on 500 mg of Catalyst (8 Torr)

Run	Adsorption (%)	Temp. (°C)	Flow H_2 (ml/min)	Product yield (%)			Distribution (mole%)								
				Saturated amine	α-Picoline	H.C.	C_1	C_2	C_3	C_4	C_5	C_6	isoC_7	nC_7	Cyclic C_7 including toluene
E1	19.4	390	15	1.3	0	13.6	22.8	8.3	13.7	12.2	3.2			23.7	16.0
E2	7.9	390	15	0.7	0.3	14.3	23.7	4.7	15.1	8.5	3.7	1.2	1.3	26.5	14.6
E3	7.3	390	50	0.2	1.3	8.1	40.8	5.7	10.1	5.3	4.0	1.4	1.0	22.2	11.2
E4	0	390	100	0.2	5.2	6.3	34.8	8.3	9.0	7.4	6.0	2.0	1.0	22.7	8.5
E14	20	250	50	0.7	0.5	0.8	5.7	0.7	1.9	5.2	7.1	—	—	67.0	12.4
E20	0	300	50	0.1	0.4	1.1	4.7	0.4	11.1	11.4	—	—	—	3.7	66.3
E27	0	300	155	—	0.1	0.7	6.8	0.7	12.4	12.0	—	—	—	11.5	45.7
E30	0	300	35	—	0.2	3.2	1.6	0.4	14.4	9.3	—	—	—	5.7	68.6
E33	0	300	170	—	0.06	0.6	1.7	0.4	19.5	12.4	—	—	—	7.1	58.7
E39	0	300	100	—	0.2	0.7	2.9	2.5	13.2	8.9	—	—	—	5.7	63.4
Eϕ15	—	390	50	—	—	2.9	18.3	29.4	13.9	7.6	3.1	7.1	3.9	—	13.3
E_{Al}	0	300	15	0	—	0.03	12	—	27	4	—	—	—	—	57

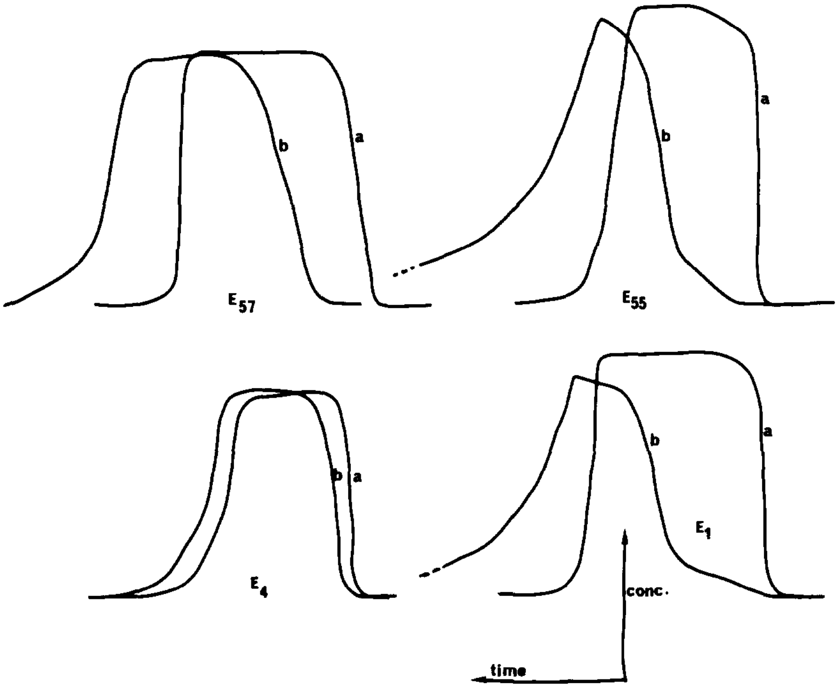
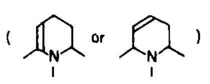


FIG. 2. Adsorption of materials on the catalyst during reaction. E1 (19.4%), fresh catalyst. E4 (0%). E55 (20.5%), catalyst kept under H_2 flow for 1 month after 54 runs. E57 (7.6%). Reaction temperature, 350°C. (a) Before the catalyst; (b) after the catalyst.

Traces of partially hydrogenated compounds were observed, mainly the monoolefine



The formation of α-picoline (or 2-methylpyridine) was important, except in E1.

The distributions of the different hydrocarbons obtained in the four reactions at 390°C were similar despite the variation of the H_2 flow which only modified the total conversion. However, in E1, only the *saturated* acyclic hydrocarbons in C_2, C_3, . . . , C_7 were formed (as in E14) with the cyclic C_7 while in E2, E3, and E4 the amount of the corresponding unsaturated hydrocarbons increased to reach 90% of these products. The formation of the saturated products (amine or hydrocarbon) occurred when the adsorption was strong. At 390°C the conversion is too high and the different hydrocarbons formed could be the result of successive reactions far from the initial distribution (see Eϕ15 showing an activity of the catalyst for the hydrocarbon n-C_7 reaction itself). Then any attempt to draw conclusions about the reaction mechanisms will be hazardous. However, it is interesting to note the important amount of cyclic C_7 formed.

In order to determine the initial distribution of the products, other reactions, E20, E27, E30, E33, and E39, were made at 300°C with different flow rates of H_2. The conversion to hydrocarbons was kept at or below 3%. The only products formed in noticeable amounts were α-picoline and three families of hydrocarbons: C_3 + nC_4, nC_7, and cyclic C_7 including toluene. The relative concentrations of the products are only a weak function of the conversion, and by means of extrapolation to conversion zero it is found that the initial relative concentrations amount to: 8% for nC_7, 21% for $C_3 + C_4$, and 60% for cyclic C_7.

We report also four reactions, F4, F8, F11, and F14, of the 2-6-lupetidine at 300°C under different flow rates of H_2 on the same catalyst. The formation of the corresponding unsaturated amines (mono-, di-, or triolefinic) was very high (43.1% in F4) while the α-pipecoline (or 2-methylpiperidine) was *never* formed. The conversion to hydrocarbons has been kept below 4.3%. The main products formed are C_3, nC_7, and cyclic C_7. Their extrapolated initial relative concentrations amount to: 4% for $C_3 + C_4$, 18% for cyclic C_7, and 69% for nC_7.

Blank experiments (E_{Al} and F_{Al}, performed under the same conditions on pure alumina show a *very poor activity* for the HDN of the aromatic compound (two orders of magnitude compared with the 12% MoO_3 catalyst) and a *strong activity* for the HDN of the saturated amine (same activity compared with the MoO_3 catalyst) with the formation of large amounts of n-C_7 olefines. However, the dehydrogenation (4.3%) is weaker than that on the MoO_3 catalyst and consequently the cyclic C_7 compounds are not formed.

DISCUSSION

The different routes proposed by McIlvried (*8*) and Sonnemans *et al.* (*9, 10*) cannot explain these results. Obviously the conditions of reaction are very different (pressure and catalyst). We detected traces of disproportionation products only for the reaction of the saturated amine, never for the aromatic one, and the sequence aromatic → hydrogenation → HDN cannot give the distributions we observed.

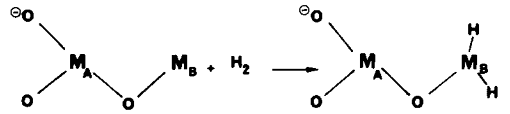
As far as our catalyst and our conditions are concerned we propose the following hypothesis. In agreement with recent results (*16, 17*), we can imagine the surface of the catalyst containing two forms of Mo atoms more or less reduced (Scheme 1) which we shall call Mo_A and Mo_B.

Analysis of our catalyst by X-ray photo-

TABLE 2

Reaction of 2-6-Lupetidine on 500 mg of Catalyst (9 Torr)

Run	Adsorption (%)	Temp (°C)	Flow (ml/min)	Product yield (%)			Distribution (mole%)								
				Unsaturated	α-Piperidine	H.C.	C_1	C_2	C_3	C_4	C_5	C_6	$isoC_7$	nC_7	Cyclic C_7 including toluene
F4	0	300	75	43.1	0	3.8	2.4	0.5	3.7	1.2	0.9	—	—	70.6	20.2
F8	0	300	170	?	0	2.1	5.3	0.4	3.1	1.1	0.9	—	—	74.0	14.2
F11	0	300	45	11.5	0	4.3	3.9	0.3	2.6	0.7	0.8	—	—	73.8	16.7
F14	0	300	150	31.4	0	2.6	3.6	0.4	3.7	1.0	0.8	—	—	64.0	21.2
F_{Al}	~0	300	15	4.3	0	2.7	—	—	~20		—	—	—	>80%	—



SCHEME 1. Site of reaction and dissociative adsorption of H_2.

electron spectroscopy shows unambiguously that several forms of more or less reduced Mo are present on the surface (*13*). No further hypothesis will be made about the surface, the nature of the site, or the physical properties of the catalyst. Schematically, Mo_B will be responsible for the hydrogenation or dealkylation reactions and will behave like a pure metal and Mo_A will be the site of the denitrogenation behaving like a classical couple Lewis acid–Brønsted base ($Mo-O^-$) catalyst.

Under the H_2 flow, the Mo_B sites dissociate hydrogen molecules to give two adsorbed hydrogen atoms (Scheme 1).

Let us now consider the different possibilities of adsorption and reaction for the 2-6-lutidine. The configuration of this molecule allows two possible forms of adsorption (*14*, *15*), one "vertical" by the nitrogen doublet and one "horizontal" by the aromatic π-electrons.

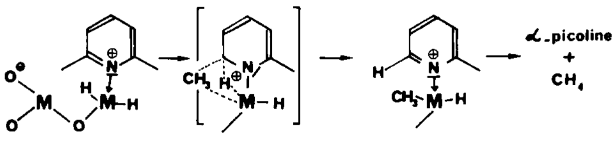
(1) The *vertical adsorption* on Mo_B leads either to the dealkylation reaction (Scheme 2) or to hydrogenation followed by denitrogenation and the formation of nC_7 hydrocarbons (Scheme 3).

(2) The *horizontal adsorption* on Mo_A leads to the cyclic C_7 hydrocarbons (Scheme 4) or to the C_3 and C_4 hydrocarbons and surface poisoning by the formation of polymers (Scheme 5). With Schemes 4 and 5 one can explain the parallelism between the formation of the $C_3 + C_4$ hydrocarbons and that of cyclic C_7 hydrocarbons; one can also explain the smaller amount of C_4 in comparison with C_3 hydrocarbons formed (Table 1) because some of the C_4 molecules are involved in the polymerisation process. The smaller amount of $C_3 + C_4$ compared to the cyclic C_7 is in agreement with the fact already observed that the rate-determining step is the hydrogenation (*8*) (two successive hydrogenations are necessary in the second reaction). The same argument can be used for the formation of the nC_7 and in the comparison with the reaction of the saturated amine.

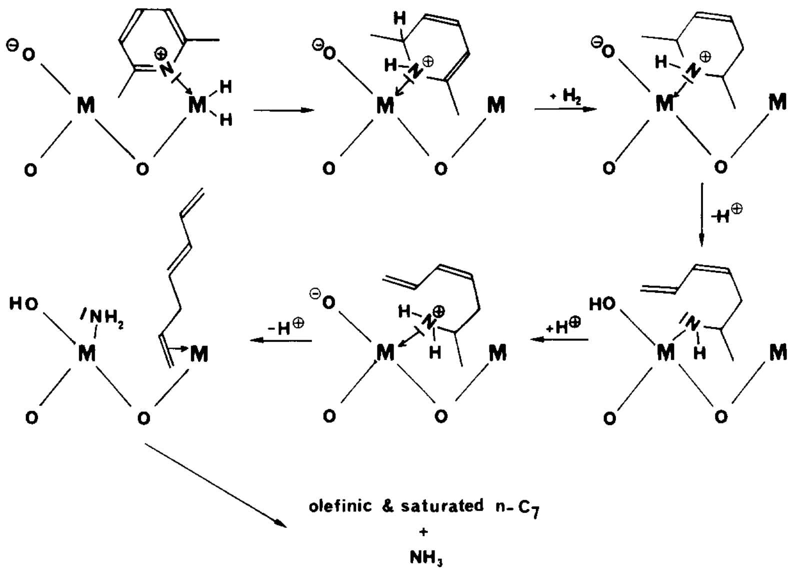
The reactions of the 2-6-lupetidine (or 2-6-dimethylpiperidine) confirm these mechanisms of reaction (Scheme 6). Vertical adsorption only is possible and, therefore, the main products formed are the nC_7 hydrocarbons (reaction (1) in Scheme 6). Reaction (2) leading to the C_3 and C_4 hydrocarbon molecules is not important probably because the rupture of a C–C bond in the cycle is harder than the C–H rupture in reaction (1). Route (3) leading to dehydrogenated amines found in large amounts (Table 2) and followed by the formation of cyclic C_7 hydrocarbons (and $C_3 + C_4$) after horizontal adsorption is important.

Finally we did not observe any dealkylation reaction. The mechanism proposed in Scheme 2 supposes a delocalization of the positive charge shared by the C–N–Mo atoms which is not possible with a saturated molecule.

The reactions made on pure alumina confirm these different schemes of reaction. The hydrogenation–dehydrogenation sites do not exist under these conditions of temperature and pressure and the reactions bound to these sites have disappeared (HDN of the aromatic compound, dehydro-



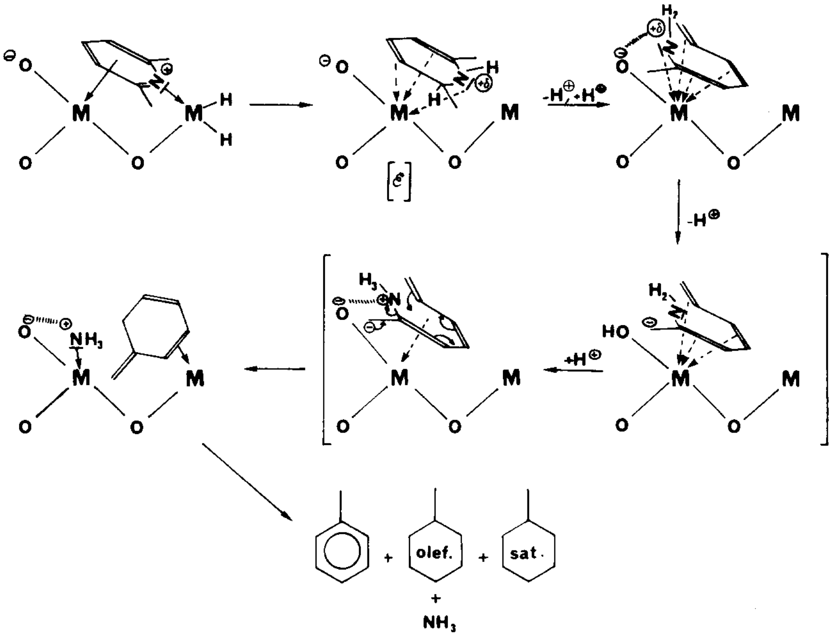
SCHEME 2. Mechanism of the dealkylation reaction. Vertical adsorption.



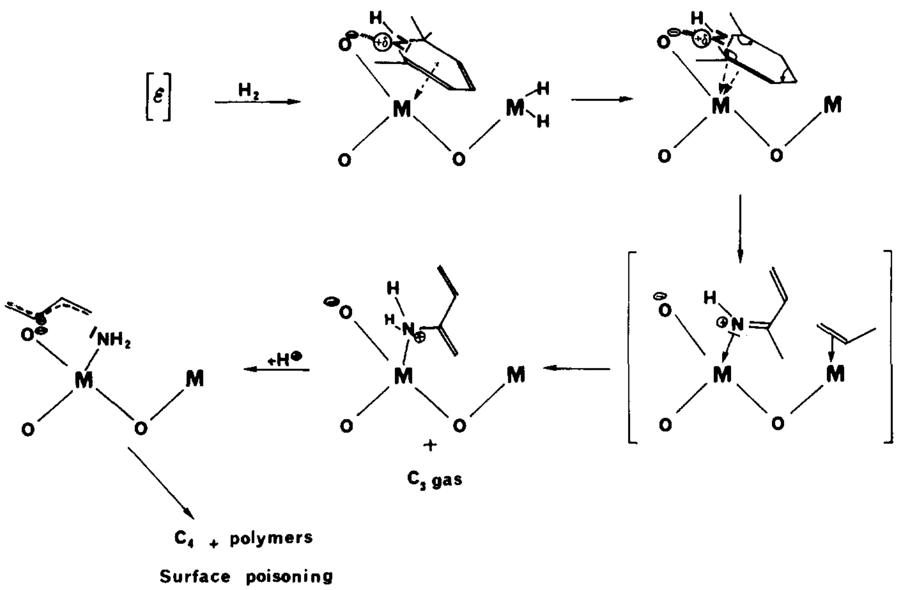
Scheme 3. Vertical adsorption. Mechanism of nC_7 hydrocarbon formation.

genation of the saturated amine, Route (3) in Scheme 6). The denitrification reaction of the saturated amine occurs to a normal extent (Routes (1) and (2) in Scheme 6).

The problem of the adsorption on fresh catalysts, bound to the formation of saturated products, is still not clear. It is not a handicap for the mechanism schemes we proposed, because the only reactions we discussed have been performed on a stabi-



Scheme 4. Horizontal adsorption. Mechanism of cyclic C_7 hydrocarbon formation.

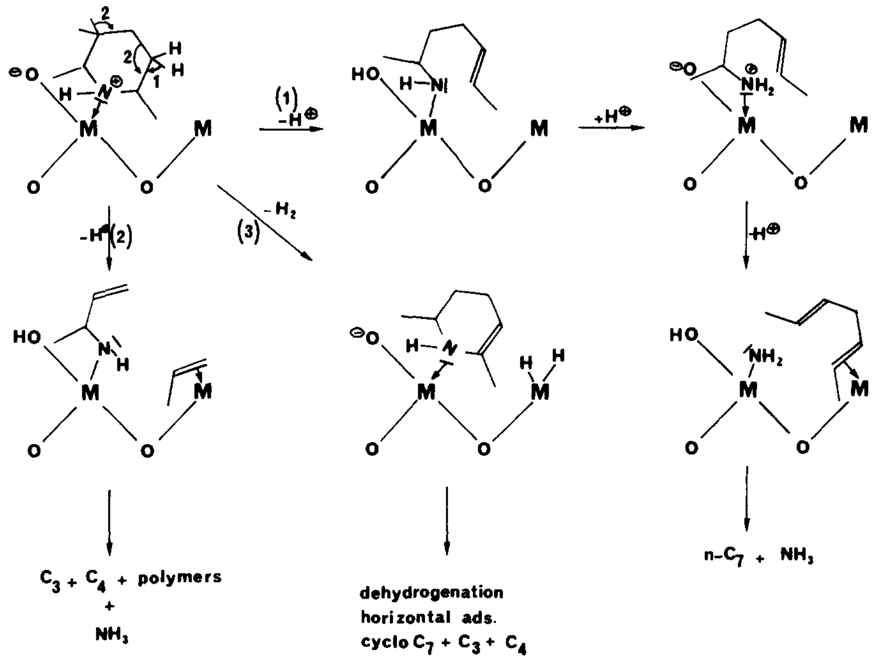


SCHEME 5. Horizontal adsorption. Mechanism of C_3 and C_4 hydrocarbon formation.

lized catalyst where the adsorption was absent.

CONCLUSION

All the different results we observed can be explained by the schemes we have proposed but at this stage they are very speculative; further experiments are necessary for confirmation. However, the distinction between a reduced site responsible for hy-



SCHEME 6. Reactions of 2-6-lupetidine.

drogenation–dehydrogenation and an oxidized site for the HDN reaction can together with the proposition of "horizontal" or "vertical" adsorption help in the understanding of the HDN reaction mechanisms.

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