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Synthesis of fatty amines. Selectivity control in presence of multifunctional catalysts

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Abstract

Fatty and *N*-methyl (or ethyl) substituted amines used, for example, for the preparation of tensioactive agents are generally obtained from the reaction of fatty acids (or esters), ammonia, light alcohols and hydrogen or nitriles, light alcohols and hydrogen over copper or nickel catalysts. In these processes, the rate-limiting step is either the light alcohol (R′OH) dehydrogenation for the formation of RNR'_2 or the secondary amine formation (R_2NH). In both cases the light alcohol and the by-product water have inhibiting effects under the rather severe experimental conditions. Over supported copper–chromite catalysts there exists a correlation between the selectivity to RNR'_2 and the presence of a well dispersed copper chromite phase stabilized with alkaline-earth elements. However, over such catalysts the R_2NR' amines cannot be obtained with high selectivity. In a second part of our study stimulated by the fact that environmental legislation will soon mandate replacements of copper–chromium catalysts with non-chromium catalysts, we investigated promoted nickel catalysts. In order to suppress the inhibiting effect of light alcohols, hexamethylene tetramine (HMTA) was used as methylating agent. Under these conditions, the nitrile is transformed either into dimethylalkylamine or into methyldialkylamine with a selectivity (or a yield) higher than 90%. Moreover, it was shown that HMTA was catalytically converted into monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) during the reaction. These reagents specially MMA, DMA act as methylating agents of primary alkylamines (RNH_2) while the corresponding imines ($CH_2{=}NH$ or $CH_2{=}N{-}CH_3$) would be the methylating species of the secondary alkylamine (R_2NH).

Keywords: Amine synthesis; Amination of acids or esters; Nitrile hydrogenation; *N*-Methylation with methanol or HMTA; HMTA hydrogenolysis; Promoted copper–chromite catalysts; Promoted nickel catalysts

1. Introduction

Aliphatic amines obtained from fatty acids or esters also known as fatty amines are generally primary (RNH_2), secondary (R_2NH or $RNHR'$) tertiary (R_3N, R_2NR', RNR'_2) amines, diamines, where R contains 8–22 carbon atoms and R′ is a short hydrocarbon chain. Most of the fatty amines are used in the preparation of surface active agents and corrosion inhibitors. Secondary fatty amines are usually derivatized to quaternary salts for use, for instance, in personal hygiene and laundry products (fabric softeners) [1–3].

The fatty acids or esters, used as raw materials, are produced from animal or vegetable oils and fats each with its own hydrocarbon chain length and unsaturation number.

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Nevertheless, depending on the country and the availability of raw materials, fatty amines can also be obtained from the petrochemical industry via oxoaldehydes or alcohols, and olefins. All these methods of preparation are presented in Table 1.

Among these processes, the amination of fatty compounds, the hydrogenation of nitriles, the amination of alcohols and *N*-alkylation are the main reactions in the industrial preparation of amines. During the last ten years, we have studied in our laboratory a continuous one-step process for the preparation of unsymmetric tertiary amines R_2NR' and RNR'_2 starting from (1) acids, esters and ammonia or (2) nitriles, hydrogen and light alcohols [4–7].

Table 1
Catalysts and processes used for amine synthesis from nitriles

Catalyst	Nitrile	Characteristics of the process	Example	Reference
Primary amines				
Ni–Mg/support	C_6-C_{24} (linear)	Batch, in the presence of NH_3 $80°C<T<200°C$, $10<P<60$ bar	Dodecylnitrile ↓ Dodecylamine (96%) T=140°C, P=16 bar	[24]
Ni or Co	C_8-C_{22} (linear, unsat.)	Batch, 2 steps in the presence of NH_3 1st step: nitrile reduction 2nd step: reduction of C=C $80°C<T<160°C$, $1<P<50$ bar	oleonitrile 135°C ↓ 35 bar oleylamine (96.7%) 140°C ↓ 1 bar stearylamine (96 %)	[25]
Raney Co promoted with Ni and Cr	Polynitrile	Continuous in the presence of NH_3 $60°C<T<125°C$ $3<P<300$ bar	adipic nitrile 125°C ↓ 65 bar HMDA (96%)	[26]
Ni/SiO_2	C_6-C_{24} (linear)	Batch, in the presence of NH_3 and NaOH T=150°C, P=50 bar	Fatty nitriles ↓ Fatty primary amines (87%)	[27]
Raney Ni	$>C_6$	Batch, in the presence of NH_3 $T\sim$125°C–140°C $P>10$ bar	Fatty nitriles ↓ Primary amines (96%)	[28]
Secondary amines				
Ni–Cu–Cr–Mo	C_8-C_{22} (linear)	Continuous, 2 steps: 1st step →primary amine in the presence of H_2 and NH_3, 2nd step→secondary amine in the presence of H_2, $130°C<T<180°C$, $3<P<300$ bar	Secondary amine (93%), T=155°C, P=30 bar	[29]
Co–Zr/support	C_8–C_{22} (linear)	Continuous, 2 steps (idem as previous case)	Secondary amine (93%), T=150°C, P=35 bar	[30]
Ni/support	C_8–C_{22} (linear, unsat.)	Batch, in the presence of $AcNH_2$ to inhibit the reaction of C=C bond, $160°C<T<200°C$, P=3 bar	Secondary amine (89%)	[31]
$Cu–Cr–K/SiO_2$	C_8–C_{22} (linear)	Continuous, $80°C<T<250°C$, $30<P<200$ bar	Secondary amine (90%), T=160°C, P=50 bar	[32]

These syntheses involve very different steps (amidation, dehydration, hydrogenation, dehydrogenation, etc.) for which multifunctional catalysts are required.

The aim of this paper is to present the results we have obtained recently over copper and nickel catalysts in the selective synthesis of $RN(R')_2$ or R_2NR' (R' being a CH_3 or C_2H_5 group).

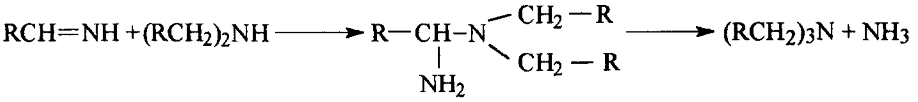
2. Reaction scheme in the formation of amines from nitriles

It is well known that the catalytic hydrogenation of nitriles produces a mixture of primary, secondary and tertiary amines. The first mechanism of this reaction was proposed by Von Braun et al. in 1923 [8] (Fig. 1).

Nitrile is hydrogenated first to an imine then to the primary amine. The primary amine can react with the intermediate imine and form the secondary amine (dialkylamine) via the formation of 1-aminodialkylamine.

A few years later, Kindler and Hesse [9] suggested that trialkylamines were formed as follows:

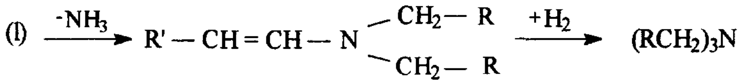
- addition of the secondary amine to the imine



$$RCH{=}NH + (RCH_2)_2NH \longrightarrow \underset{\displaystyle NH_2}{R{-}\underset{|}{C}H}{-}N\begin{matrix} CH_2{-}R \\ CH_2{-}R \end{matrix} \longrightarrow (RCH_2)_3N + NH_3 \qquad (1)$$

gem diamine (I)

Greenfield in 1967 suggested that NH_3 is first eliminated from the gem diamine (I) to form an intermediate enamine (II) [10];



$$(I) \xrightarrow{-NH_3} R'-CH=CH-N\begin{matrix} CH_2-R \\ CH_2-R \end{matrix} \xrightarrow{+H_2} (RCH_2)_3N \qquad (2)$$

More recently Volf and Pasek [11] confirmed the above hypothesis for the formation of trialkylamine and that the secondary amine was formed via the imine rather than a direct hydrogenolysis of the first aminodialkylamine. The

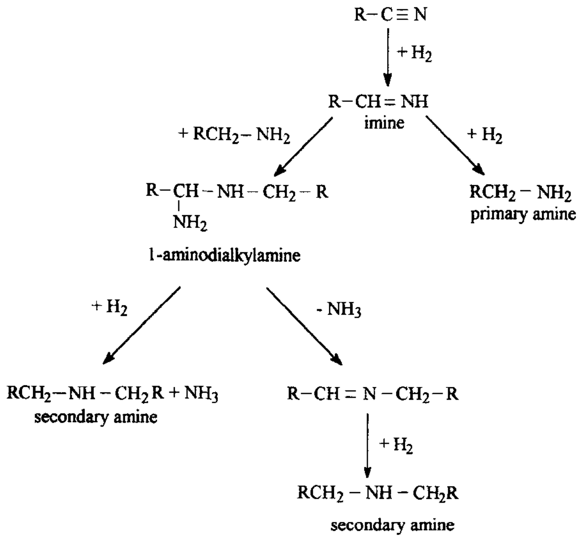


Fig. 1. Reaction scheme in nitrile hydrogenation [8].

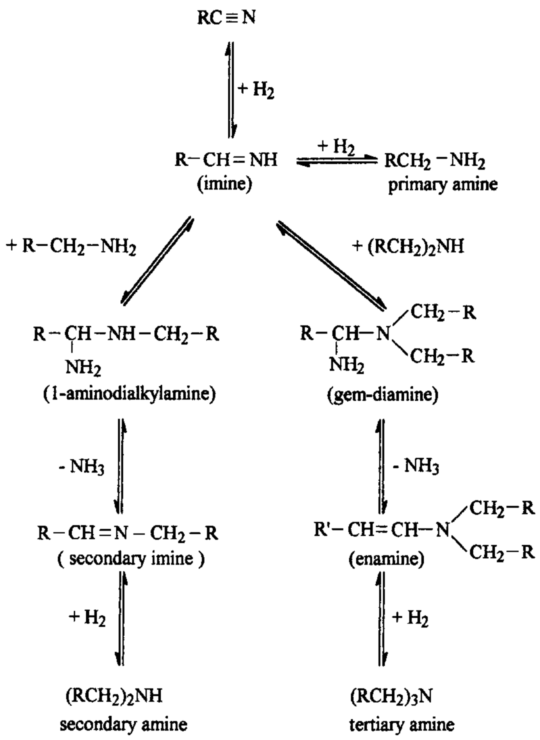


Fig. 2. Reaction scheme in nitrile hydrogenation [11].

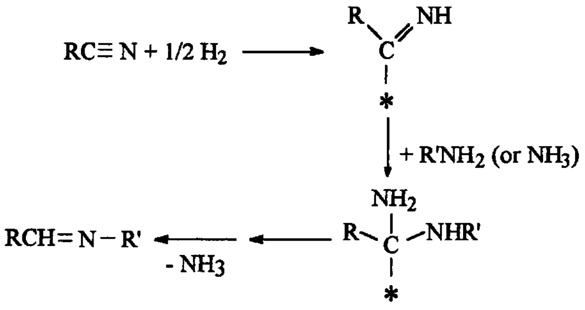


Fig. 3. Intermediate step in nitrile hydrogenation [12].

following reaction scheme was proposed (Fig. 2) [11]. Nevertheless, most of the intermediates (except the primary imine) remained unidentified at that time.

Dallons et al. [12] who had not observed the presence of these intermediates suggested that some of these compounds, like 1-aminodialkylamine, could only be formed in the adsorbed state at the surface of the catalyst (Fig. 3).

Suppo-Essayem, when studying the synthesis of unsymmetric fatty tertiary amines (R_2NR') separated and identified the main intermediate imines and enamines proposed in the reaction scheme of Volf and Pasek (Fig. 2) [13].

In a recent work on the reaction mechanism of light amines synthesis over metal-supported catalysts, Verhaak [14] defined the pathway of nitrile hydrogenation (Fig. 4): “On the metallic component of the catalyst, nitriles are hydrogenated to imines and amines. These compounds then migrate to acidic sites where the imines are protonated

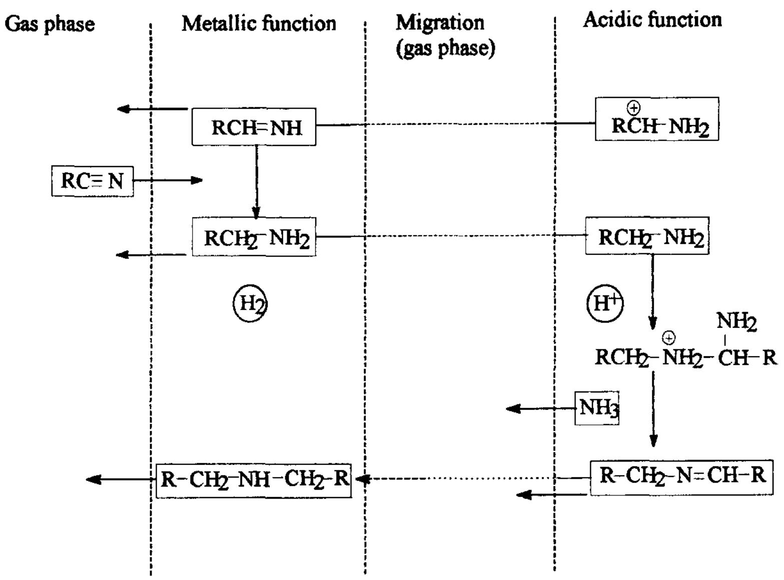


Fig. 4. Bifunctionality in hydrogenation of nitriles [14].

and react with amines coming from the gas phase. The "α amino amine" is then deprotonated and loses ammonia. A Schiff base is found that after desorption from the support migrates back to the metal, where it is hydrogenated to the secondary amine".

Although this reaction scheme has been proposed for the preparation of light amines (C_3–C_4), a similar pathway could be valid in the synthesis of fatty amines. Nevertheless, diffusional effects due to the high molecular weight of fatty compounds and the modification of the catalyst surface with reagents or products could change the nature of the rate-limiting steps, the active sites and the selectivity [13,15].

3. Catalysts suitable for the hydrogenation of fatty nitriles

The catalyst is the determining factor in the selectivity of nitrile hydrogenation and various solids are reported to be effective for these reactions. Two types of materials, bulk and supported, containing a metal – nickel, cobalt, copper, rhodium, platinum or palladium – were used. Nickel and cobalt catalysts are generally used for the synthesis of primary amines [10,16]. Different promoters, such as chromium [17] or boron [18], have been proposed to increase the primary amine selectivity. However, the acidity of the support influences the selectivity. The formation of secondary and tertiary amines increases with the number and the acid strength of the active sites [19,20]. Copper–chromite catalysts promoted with alkaline or alkaline-earth compounds like rhodium catalysts [21] could be used for the secondary amine synthesis [13]; but the support could have a definite effect on the final catalytic properties [12].

Platinum and palladium are quite selective to tertiary amines [10,22], however, for all the above mentioned catalysts, the support can modify both the activity and the selectivity of these metals [23].

Table 1 gives the main characteristics of certain processes describing the preparation of primary or secondary amine over copper, nickel or cobalt catalysts.

However, when the reactions are carried out in a slurry (triphasic) reactor, a solvent added to the medium can often modify greatly the catalytic properties of the metals. Thus, besides a solvation effect or/and a modification of the surface coverage, other phenomena such as mass or heat transfer, limitations, catalyst modification or poisoning could be involved. The hydrogenation of nitriles over Raney nickel in the presence of alcohols has shown this inhibiting effect of methanol [33]. In fact, this effect is a result of the partial poisoning of the catalyst with "formaldehyde species" originating from the methanol decomposition over nickel particles [33]. This poisoning effect produced by methanol has been also mentioned in the case of platinum or palladium catalysts used for nitrile hydrogenation [10]. Water can suppress this effect [10,34].

Above 250°C, water as well as ammonia can poison copper and nickel catalysts [5]. All these results show that even if the hydrogenation of nitriles is a complicated process comprising several competitive reactions, it is possible, with an appropriate choice of the metal, support and reaction conditions, to obtain selectively the primary (RNH_2), the secondary (R_2NH) or the tertiary amine (R_3N). The modification of active centres or/and of the kinetic parameters influence the reactivity of intermediates (aldimines, alkylidenealkylamines, enamines) and the rates of hydrogenation and condensation (Fig. 2).

Such amine synthesis means that:

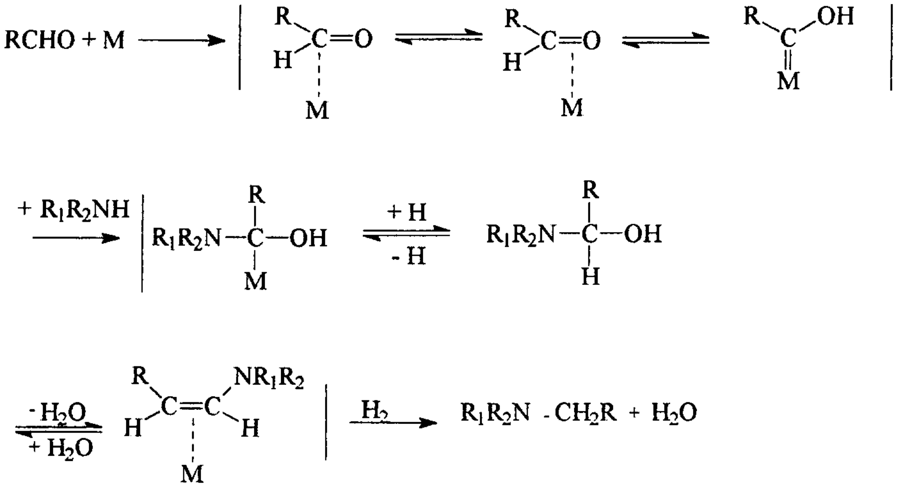
(i) The industrial process is a three-step reaction when starting from natural fats: (a) hydrolysis of fats to acids, (b) amination of acids into nitriles and (c) hydrogenation–condensation of nitriles. An improvement of the process could be the direct conversion of acids (or methyl esters) into amines.

(ii) The alkylamines are the most valuable products. In fact, other compounds such as unsymmetric amines R_2NR' or RNR'_2 (where R and R′ are, respectively, fatty and short hydrocarbon chains) are important for the preparation of active surface agents. These amines can be obtained from the reactions of nitriles with light alcohols or directly from acids (or methyl esters), ammonia, light alcohols in the presence of multifunctional catalysts.

4. Synthesis of unsymmetric amines (R_2NR' or RNR_2') from acids, esters or nitriles

A significant number of amines is used for the preparation of tensioactive agents (i.e., quaternary ammonium salts). The specific properties of these compounds (for example, H.L. Balance) depend on the hydrocarbon chain length of the *N*-substituents. For example a few years ago fabric softener formulations were based largely on DHTMAC (Di. (hydrogenated) tallow dimethylammonium chloride: $R_2N^+(CH_3)_2X^-$ where $R=C_{18}$, $X^-=Cl^-$) [3]. So the production of such softeners (now constant) needs the preparation of an unsymmetric amine "$(C_{18})_2NCH_3$" and more generally the selective synthesis of R_2NR' or RNR'_2.

The first steps of these processes are similar to those already described. The last step, the *N*-alkylation of primary or secondary amines with light alcohols, involves the alcohol dehydrogenation and the addition to the amines of the resulting carbonyl species (Scheme 1).



Scheme 1.

Table 2
Catalysts for amine methylation

Catalyst	Amine	Methylating agent	Characteristics of the process	Example	Reference
CuO–Cr_2O_3	Secondary amine	CH_3OH	Batch, CH_3OH in excess without hydrogen; 350–450°C, 70 bar	Dioctadecylamine $+CH_3OH \rightarrow R_2NCH_3$ (98%)	[38]
Metal oxides	RR′NH, R=C_8–C_{22}, R′=H or C_1–C_{22}	CH_3OH	Flow, 250°C–300°C, 7–84 bar		[39]
Raney Ni	Nitrile or unsatured amine, C_8–C_{22}	$HCHO+H_2$	Batch, three steps: (1) secondary amine synthesis, (2) methylation, (3)reduction, 150°C–230°C, 1–10 bar	R_2NCH_3 (92%)	[40,41]
CuO–ZnO soluble alkaline salts	NH_3 or amines	$(CO+H_2)$	Flow, 150°C–300°C, <100 bar	Light amines	[36]

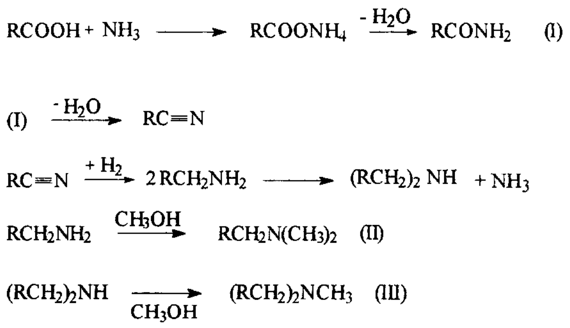
Methanol is used largely for the methylation of different types of amines under severe conditions. This process replaces the homogeneous methylation reaction in which formaldehyde is associated with formic acid (Leuckart–Wallach reaction) (Table 2).

$$RNH_2 + 2HCHO + 2HCO_2H \rightarrow RN(CH_3)_2 + 2CO_2 + 2H_2O \qquad (3)$$

$$R_2NH + HCHO + HCO_2H \rightarrow R_2NCH_3 + CO_2 + H_2O \qquad (4)$$

Syngas (CO, H_2) [35,36] or dimethyl carbonate [37] can also act as methylating agents. Therefore, if we want to improve these amine syntheses and perform the reaction in one or two steps starting from acids (esters) or nitriles, we must use multifunctional catalysts stable in the presence of water and ammonia (Scheme 2).

To obtain selectively (II) or (III), firstly we studied copper catalysts, essentially the effect of the support and of the alkaline promoters and the stability of these catalysts in the presence of water and ammonia. Secondly, in order to replace chromium and eliminate certain problems concerning the recycling of used catalysts, promoted nickel catalysts were studied. Lastly, the methylating agent was also replaced and HMTA was proposed for the methylation of amines.



Scheme 2.

5. Synthesis of dimethylalkylamines over copper catalysts

5.1. *From fatty acids or esters*

5.1.1. *Effect of the support*

Table 3 shows that methyl dodecanoate is easily converted into amine in the presence of copper–chromite species deposited on alumina or on titania. One can observe that the difficult methylation reaction is favoured by alumina. Moreover, a significant increase of *N*-dimethyldodecylamine is obtained when the reaction is carried out with a large excess of hydrogen. Because of the mechanism of the reaction, this is unexpected. It is generally accepted that methylation of the primary amine with methanol requires (i) the dehydrogenation of alcohol to a carbonyl compound and (ii) a further reaction of this compound with a primary or a secondary amine via imine or enamine intermediates [42–44].

This hydrogen effect can be explained by the low hydrogen coverage which, under normal conditions, is not sufficient to maintain the catalyst in the adequate reduced state and to inhibit the formation of carbonaceous deposits (the modification of the catalyst) or the strong adsorption of certain reagents and products.

5.1.2. *Effect of Ca and Mn additives on the catalytic properties of $CuCr/Al_2O_3$ (TiO_2)*

To increase the rate of the methylation steps, we studied the effect of the addition of base promoters to the above mentioned catalysts. The effect of adding Ca or Mn to $CuCr/Al_2O_3$ (TiO_2) catalysts, presented in Table 4, demonstrate that the selectivity in *N*-dimethyldodecylamine is much enhanced and that the effect is more significant with alumina than with a titania support. Moreover, the total amine selectivity with a promoter is

Table 3

Amination and *N*-methylation of methyldodecanoate ($C_{11}H_{23}COOCH_3$) in the presence of copper–chromite catalysts

Catalyst (wt %)	Conversion ester (%)	Selectivity (%)						
		RNH_2	$RNHCH_3$	$RN(CH_3)_2$	R_2NH	R_2NCH_3	R_3N	Others
20 Cu–20 Cr/TiO_2	97.5	31.9	30.7	20.0	2.5	2.0	2.0	10.7
idem (a)	90.0	5.2	16.5	61.0	1.5	3.5	2.0	9.9
10 Cu–10 Cr/Al_2O_3[a]	84	12.3	30.4	36.6	—	2.6	—	18.3

P=50 bar, T=250°C, $(LHSV)_{ester}$=1/6 h^{-1}, ester/NH_3/CH_3OH/H_2=1/10/40/50 (molar).
(a) Ester/NH_3/CH_3OH/H_2=1:10:40:100 (molar).

Table 4

Effect of promoters in the amination of dodecanoic acid

Catalyst composition (wt%)	Acid or ester conversion (%)	Selectivity (%)				
		RNH_2	$RNHCH_3$	$RN(CH_3)_2$	$RCOOCH_3$	Others
Reaction: acid/NH_3/CH_3OH/H_2						
43 CuO–39 Cr_2O_3	100	21.2	26.0	37.1	7.0	8.7
15 Cu 15 Cr–Al_2O_3	100	20.0	32.4	26.0	8.0	13.6
15 Cu 15 Cr 2 Ca–Al_2O_3	100	8.4	24.0	67.0	—	0.6
15 Cu 15 Cr 2 Mn–Al_2O_3	100	16.0	36.0	46.0	—	2.0
15 Cu 15 Cr 2 Ca–TiO_2	100	27.0	31.0	35.6	2.1	4.3
Reaction: ester/NH_3/CH_3OH/H_2						
15 Cu 15 Cr 2 Ca–Al_2O_3	100	10.0	20.8	65.7	—	3.5

P=50 bar, T=300°C, $(LHSV)_{acid\ or\ ester}$=1/6 h^{-1}, acid (or ester)/NH_3/CH_3OH/H_2 =1:10:40:100 (molar).

Table 5
Hydrogenation and *N*-methylation of dodecylnitrile ($C_{11}H_{23}CN$) and *N*-methylation of dodecylamine ($C_{12}H_{25}NH_2$) in the presence of a copper–chromite catalyst

Reagent	Conversion (%)	Selectivity (%)						
		RNH_2	$RNHCH_3$	$RN(CH_3)_2$	R_2NH	R_2NCH_3	R_3N	Others
$C_{11}H_{23}CN$	100	2.0	12.9	78.0	2.7	2.9	1.5	—
$C_{12}H_{25}NH_2$	100	—	7.3	83.3	0.8	0.9	1.9	5.8

Catalyst composition (wt %): 20 Cu 20 Cr/TiO_2, P=50 bar, T=250°C, (LHSV) reagent=1/6 h^{-1}, reagent/CH_3OH/H_2=1:10:50 (molar).

particularly high, over 98% instead of 80%. A similar result (Table 4) is obtained with methyl dodecanoate instead of with dodecanoic acid.

These results show clearly that over promoted and supported copper–chromium catalysts, fatty acids and esters are transformed selectively into dimethylalkylamines [45]. Nevertheless, owing to certain modifications of the catalysts during the reaction or inhibiting effects of the reagents and the products [5], the reaction must be performed in the presence of a large excess of hydrogen. Moreover, even under these conditions, the rate of the formation of substituted amine is rather low (see LHSV in Tables 3 and 4).

5.2. *From nitriles*

The reactivities of dodecylnitrile or dodecylamine measured under the same experimental conditions (Table 5) show that nitrile and the primary amine are much more easily transformed into *N*-dimethylalkylamine than either the ester or the acid (Tables 3 and 4). The rate determining step in the methylation process is one of the first reactions which convert the ester or the acid into nitrile. These results confirm that the adsorption of the reagent is not quite effective on the catalyst or/and that the water formed during the reaction could lead to a superficial (or a bulk) modification of the catalyst and of the adsorption properties of certain reagents [5,13].

To determine the main characteristics of these reactions and particularly the effects of the catalyst composition, the roles of the support and promoters were also investigated.

Table 6 gives the results obtained with CuCr catalysts supported on alumina or graphite and reduced with hydrogen at 373 or 623 K. In the presence of Cu–Cr/alumina reduced at low temperature we noticed that didodecylamine was the major product while with unreduced Cu–Cr/graphite methylation reactions were preponderant (Selectivity [$RN(CH_3)_2$+$RNHCH_3$+R_2NCH_3]=75%).

After a reductive treatment of the Cu–Cr/Al_2O_3 catalyst with hydrogen at 623 K, the rate of methylation reactions and the alkylation into tridodecylamine increased significantly. Over the Cu–Cr/graphite catalyst reduced

Table 6
Conversion of lauronitrile in the presence of copper–chromium catalysts (effect of support and reduction treatment)

Catalyst composition (wt%)	Nitrile conversion (%)	Selectivity (%)					
		$RNHCH_3$	$RN(CH_3)_2$	R_2NCH_3	R_2NH	R_3N	Others
5.4 Cu 5.6 Cr/Al_2O_3[a,d]	95	5	15	30	22	20	8
5.4 Cu 5.6 Cr/Al_2O_3[b,d]	90	18	5	15	48	5	9
5.9 Cu 4.1 Cr/graphite[a,d]	95	2	3	15	15	60	5
5.9 Cu 4.1 Cr/graphite[c,d]	95	10	45	20	5	12	8

T=523 K, P=50 bar, RCN/CH_3OH/H_2=1:10:50 (molar), LHSV=0.5 h^{-1}.

[a] Reduction at 623 K.

[b] Reduction at 373 K.

[c] No reduction.

[d] Catalytic results obtained after 25 h experiment.

Table 7
Reaction of lauronitrile in the presence of methanol and hydrogen over graphite supported catalysts

Catalyst composition (wt%)	Reaction time (h)	Nitrile conversion (%)	Selectivity (%)					
			RNHMe	$RNMe_2$	R_2NH	R_2NMe	R_3N	Others
5.5 Cu 4.2 Cr 1.7 Ba[a]	5	90	1	40	2	45	11	—
	20	95	3	35	3	45	11	—
5.8 Cu 5.0 Cr 1.2 Ba[b]	3	75	—	97	—	—	1	—
	5	85	—	85	—	—	12	2
	25	90	—	66	—	—	30	3

Experimental conditions: see Table 6.

[a]Catalyst obtained from the impregnation of a barium salt on a copper–chromite catalyst.

[b]Catalyst obtained from the coprecipitation of mixed hydroxides.

under the same conditions, mainly tridodecylamine could be observed (60%). It can be seen that the methylation of dodecylamine or of didodecylamine is favoured when the reduction rate of the catalyst is low but not so for the formation of the tridodecylamine.

On the other hand, we noticed a significant change of the conversion of dodecylnitrile and the selectivities of the main reaction products as a function of the reaction time. For both catalysts a substantial decrease in selectivity in $RN(CH_3)_2$ could be generally observed (more marked for the alumina supported catalyst than for the graphite supported). At the same time the selectivities in R_2NH and in R_2NCH_3 increased, which indicates that the condensation reaction of dodecylamine was faster than the hydrogenation and the methylation reactions.

The properties of copper–chromite catalysts can be much modified by the presence of additives such as barium [13,46]. The selectivity however depends a great deal on the content and the localization of this promoter. Indeed we observed that the modification of a Cu–Cr/graphite catalyst performed by impregnation by barium led to a different selectivity from the one obtained with a CuCrBa catalyst coprecipitated in the presence of graphite (Table 7). In both cases, if a very substantial increase of the methylation reactions (after stabilization) could be observed, the CuCrBa catalyst was much more selective for dimethyldodecylamine (72%) than the CuCr/graphite catalyst which gave equivalent amounts of this amine and methyl didodecylamine.

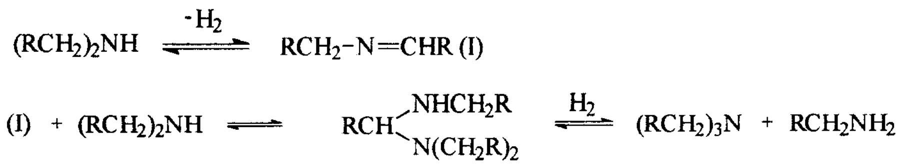
Furthermore, Table 7 shows that the selectivity of the CuCrBa/graphite catalyst still changed during the reaction, in particular, at the beginning. In the first hours the catalyst was very selective for the formation of dimethyldodecylamine ($\geq$95%). This selectivity dropped to 65% after 25 h of reaction while the formation of methyldidodecylamine increased. This result shows that the hydrogenating properties of the catalyst changed during the reaction.

Table 8
Oxidation state of surface copper and chromium species

Catalysts	Binding energy (eV)		I_{sat}/I_{mp}	$\frac{Cu^{I/0}}{Cu\ total}$ (%)	Cu binding energy (eV) Auger		Cr^{VI}/Cr total (%)
	Cu^{II}	$Cu^{I/0}$					
$CuCr/AlO_3$[a]	934.7	932.5	0.77	21	—	—	47
$CuCr/AlO_3$[b]	—	931.9	—	100	918.9	Cu^0	ϵ
$CuCrBa/AlO_3$[a]	933.9	932.1	0.5	19	—	—	46
$CuCrBa/AlO_3$[b]	—	932.1	—	100	918.2	Cu^I, Cu^0	ϵ
CuCr/ Graphite[a]	934.3	932.1	0.7	45	916.2	Cu^I	34
CuCrBa/Graphite[b]	934.0	931.8	0.64	46	916.6	Cu^I	ϵ

[a]Not reduced.

[b]Reduced at 623 K.



Scheme 3.

The XPS characteristics, presented in Table 8, show that the surface composition of the catalysts depended greatly on the support and on the addition of Ba.

For alumina supported catalysts, in the presence of barium, copper oxide was not entirely reduced with hydrogen at 623 K. By contrast, only Cr^{III} species could be observed after reduction. For graphite supported catalysts the Cu^{I} content was much greater, especially in the presence of barium which, on the contrary, inhibited the formation of Cr^{VI} species even without a reduction treatment.

The main characteristic of graphite supported catalysts promoted with barium is the significant formation of a surface copper chromite phase ($CuCrO_2$) which confirms the bulk characterization [5].

We can then conclude that:

(i) The amination and specially *N*-methylation of primary and secondary amines are favoured by the presence on the surface of the catalyst of a copper chromite ($CuCrO_2$) phase stabilized by a well-chosen promoter. All the procedures of preparation and of pretreatment of graphite supported catalysts corroborate this behaviour.

(ii) The increase in the acidity of the support and the presence of Cr^{VI} species favour the production of the dialkylamine (i.e., didodecylamine) resulting from the condensation of a primary amine with the corresponding imine.

(iii) The formation of tridodecylamine, which is also enhanced by the increase of acidity of the catalyst, is also unexpectedly increased by the presence of metallic copper. A simple alkylation reaction alone cannot explain this reaction. We suggest that besides this reaction, tertiary amine could also be formed from a transalkylation reaction of the secondary amine via secondary imine and diamine intermediates (Scheme 3).

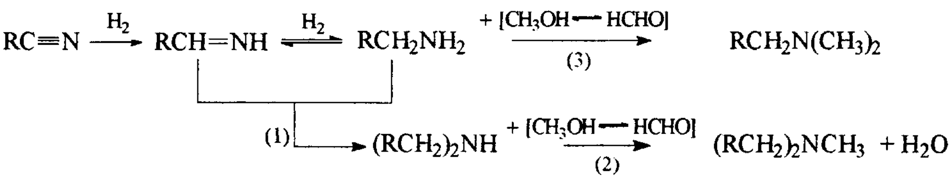
6. Synthesis of methyldialkylamines from nitriles over copper or nickel catalysts

The main reaction steps involved in the synthesis of methyldialkylamines (as represented in the preceding paragraph) are the following (Scheme 4):

The rate of the condensation step (1) must, therefore, be faster than the rate of the methylation step (3).

Over copper catalysts, the above results have shown that this could be obtained by changing the catalyst's acidity. A specific study on the role of the support over the properties of copper–chromium catalysts showed that the selectivity decreased in the following order [13]

Support	SiO_2–Al_2O_3	≈	Al_2O_3	>	SiO_2	≈	graphite	≈	ZnO
$(R_2NH + R_2NCH_3)(\%)$	56		50		30		30		30



Scheme 4.

Table 9
N-Ethylation of didodecylamine with ethanol

Catalyst	Initial rate[a]	Time (h)	R_2NH conversion (%)	Selectivity (%)	
				$R_2N–C_2H_5$	Others
E106P[c]	3.1×10^{-2}	75	50	100	0
10 Ni/graphite	1.0	3	100	77	23[b]

[a] Expressed in mol h^{-1} g^{-1} $_{cat}$($\times10^3$), T=140°C, P=1 bar.
[b] R′CN (5%), RNH–Et+$RNEt_2$ (6%), R_3N (6%), others (6%).
[c] Mallinckrodt catalyst: 80 m^2 g^{-1}; Cu/Cr/Ba=1:1:0.1 (atom).

But in most cases the rate of the methylation step was too slow and we observed a significant formation of by-products.

6.1. *Influence of the metal*

In the preliminary experiments carried out at low pressure, when we examined the *N*-alkylation of nitriles, primary amines or dialkylamines with light alcohols, we observed that there was no *N*-methylation with methanol either over a copper–chromite or over a nickel catalyst [47].

Ethyldidodecylamine, [$(C_{12}H_{25})N–C_2H_5$], was obtained selectively (Table 9), showing that the reactivity of ethanol was higher than that of methanol, and this was certainly due to the faster rate of dehydrogenation of ethanol.

The activity of a nickel catalyst was 30 times greater than that of a copper catalyst. However, the selectivity of nickel/graphite was lower than that of copper (77% as against 100%), mainly because didodecylamine was converted into dodecylamine.

To demonstrate the role of alcohol dehydrogenation in the reaction, we investigated *N*-alkylation of didodecylamine with ethanal in the presence of both catalysts (Table 10).

Compared to the results in Table 9, the initial rate of *N*-ethylation of didodecylamine over the copper catalysts was more than 30 times faster with CH_3CHO than with C_2H_5OH whereas with the nickel catalyst the initial rate with CH_3CHO was only twice faster than with C_2H_5OH. There was a significant formation of by-products which means that this catalyst was modified during the reaction.

Starting from dodecylnitrile (instead of didodecylamine) and ethanol over the same nickel catalyst, we observed a rapid formation of dialkylamine but the ethylation step was slow [47,48].

In spite of this difference, nickel catalysts remain more active. This reason plus the fact that the coming environmental legislation will soon be requiring that nickel catalysts take the place of copper–chromium catalysts, incite us to undertake already the study of nickel catalysts in the synthesis of methyl (or ethyl) dialkylamines.

Table 10
N-Ethylation of didodecylamine with ethanal over a 10 Ni/graphite catalyst

Initial rate of reaction[a]	Time (h)	R_2NH conversion (%)	Selectivity (%)						
			R′CN[c]	RCO_2Et	RNHEt	$R_2N(Et)_2$	R_2N–Et	R_3N	Others[b]
2.0	1	62	0	25.2	11.3	0	57.9	2.2	3.4
	3	83.4	12.7	17.5	11.9	2.9	53.1	1.9	0
	7	95	18.5	9.1	10.7	5.7	53.8	2.2	0

[a] See Table 9.
[b] $(C_{12}H_{25})_2N–CH{=}CH–C_{10}H_{21}$.
[c] R=R′CH_2.

Table 11
N-Methylation of didodecylamine with methanol over a nickel catalyst[b]

Initial rate of reaction[a]	Time (h)	R_2NH conversion (%)	Selectivity (%)			
			R'CN[c]	$RN(CH_3)_2$	$R_2N–CH_3$	R_3N
1.3	1	59	0	7	86	7
	4	100	8	10	72	10

[a] See Table 9.
[b] Catalyst from Engelhard (5256P).
[c] Idem Table 10.

Table 12
Hydrogenation and N-methylation (with methanol) of dodecylnitrile over of a nickel catalyst[d]

Initial rate of reaction[a]	Time (h)	Nitrile conversion (%)	Selectivity (%)						
			RNH_2	$RN(CH_3)_2$	Imine[b]	R_2NH	$R_2N–CH_3$	Enamine[c]	R_3N
4	1.5	98.3	—	3.1	1.3	86.7	6.3	2	0.6
	5.5	100	4.8	14.3	1.1	11.9	55.6	12.3	—
	7	100	7.4	17.8	0.9	0.9	61.1	11.9	—

[a] See Table 9.
[b] $C_{12}H_{25}N{=}CH–C_{11}H_{23}$.
[c] See Table 10.
[d] Catalyst from Engelhard (5256P).

6.2. *Methyldidodecylamine from nitrile, methanol and hydrogen over nickel catalysts*

Based on results obtained with copper and nickel–graphite catalysts [49] we performed the reactions with unsupported nickel/nickel oxide catalysts promoted with calcium oxide or magnesium oxide. First from didodecylamine, a significant N-methylation rate was observed and a yield of about 75% for R_2NCH_3 was obtained over a nickel catalyst promoted with magnesium oxide (Table 11).

Starting from dodecylnitrile, the activity of the nickel (5256P) was greater (Table 12). The secondary amine (R_2NH), readily formed with a selectivity of over 90%, was rapidly methylated with a selectivity of about 62%. But a disproportionation reaction occurred, leading to the enamine (c) or the trialkylamine like for copper catalysts;

$$2R_2NH \rightarrow RNH_2 + R_3N \qquad (5)$$

and dimethyldodecylamine (from the methylation of dodecylamine).

Despite a significant increase of both the activity and the selectivity for the methyldidodecylamine, one noticed, like for copper catalysts, a poisoning of the nickel sample during the reaction (certainly due to the presence of water) and an inhibiting effect of the methanol. These two negative effects led us to investigate different methylating agents such as HMTA.

6.3. *Methyldidodecylamine synthesis from nitrile, HMTA and hydrogen*

The literature propose dimethylcarbonate [50], syngas [35] or hexamethylenetetramine (HMTA) [51] as methylating agent reactions. HMTA which has numerous other applications is potentially the most appropriate compound. It was recently used for the N-methylation of nitriles and amines over a nickel catalyst [51]. In our laboratory, we studied the reactivity of HMTA with different nitrogen compounds over solid catalysts for the purpose of increasing the selectivity and to determine the substitution mechanism as well as the nature of the active sites.

Table 13
N-Methylation of dodecylnitrile with HMTA or methanol over a nickel catalyst[c]

Methylating agent	Reaction time	Nitrile conversion (%)	Selectivity (%)							
			RNH_2	$RNH–CH_3$	$RN(CH_3)_2$	Imine[a]	R_2NH	$R_2N–CH_3$	R_3N	Enamine[b]
CH_3OH	1	30	18	—	—	74.9	3.2	—	—	3.9
	46	99	9	—	0.8	3.9	81.3	—	—	5
HMTA	1	38	—	15.6	43.8	23	8.6	5.2	—	3.8
	7	100	—	—	69.4	—	9.2	21.1	0.3	—

$W_{cata}=0.2$ g; $V_{CH3OH}=2$ ml or $W_{HMTA}=7.5$ g; $V_{R'CN}=3.9$ ml; $V_{dodecane}=65$ ml; $F_{H2}=2\,l\,h^{-1}$; $T=140$°C.
[a] $C_{12}H_{25}N{=}CH–C_{11}H_{23}$.
[b] $(C_{12}H_{25})_2N–CH{=}CH–C_{10}H_{21}$.
[c] Catalyst from Engelhard (5256P).

6.3.1. N-methylation of dodecylnitrile with methanol or HMTA

Over the same nickel catalyst, the results presented in Table 13 show that the reaction rates are much faster when using HMTA instead of CH_3OH.

Moreover, owing to the change of the product distribution versus reaction time also given in Table 13, we can observe that in the presence of methanol, the imine is the main product at the beginning of the experiment. Imine is then slowly hydrogenated to didodecylamine via the enamine $[(C_{12}H_{25})_2N–CH{=}CH–C_{10}H_{21}]$. These results confirm that the rate of the methylation step with methanol is very slow.

With HMTA, dimethyldodecylamine is the main product (70%), and methyldidodecylamine, the main by-compound (30%). In this case, the methylation of primary amine is faster than the formation of R_2NH (and of $R_2N–CH_3$). But if the reaction occurs at a lower temperature, didodecylamine and methyldidodecylamine become the major products (Table 14).

As we have shown, the secondary amine was obtained mainly from the nitrile (in the absence of HMTA) over the same catalyst [7,47] and a better selectivity was obtained in this way.

First the nitrile hydrogenation was carried out at 140°C in order to obtain a yield of about 95% for R_2NH, then HMTA was added to the reaction mixture and the amine (R_2NCH_3) was obtained with a yield of about 90% (Fig. 5).

6.3.2. Mechanism of N-methylation with HMTA

First of all, the main products of the transformation of HMTA alone or in the presence of dodecylnitrile were identified. Light amines and ammonia were formed from HMTA via the following reactions (Scheme 5), but monomethylamine (MMA) and dimethylamine (DMA) were also converted into trimethylamine (TMA);

Table 14
N-Methylation of dodecylnitrile with HMTA

Temperature (°C)	Time (h)	Nitrile conversion (%)	Selectivity (%)					
			RNH_2	$RNH–CH_3$	$RN(CH_3)_2$	R_2NH	$R_2N–CH_3$	Others
80	1	31.5	31.4	—	3.4	24.3	4.3	36.6
	23	100	—	1.2	7.8	59.9	24.1	7
100	1.5	65.8	16.3	4.2	10.5	39	13.1	16.9
	23	100	—	—	21.1	8.8	65.6	4.5

For experimental conditions see Table 13.

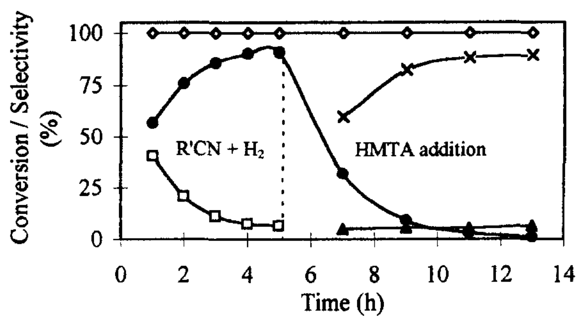
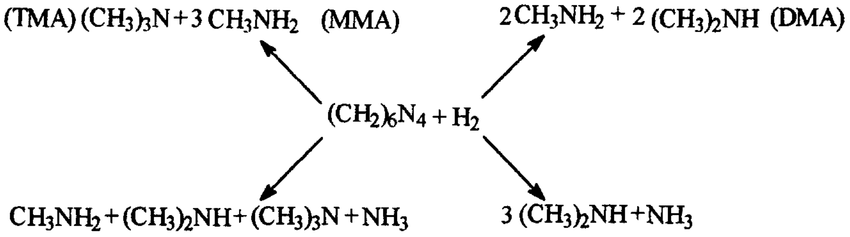


Fig. 5. Hydrogenation and *N*-methylation of dodecylnitrile with HMTA. Conversion: (◇) – R'CN ; Selectivity: (●) – R_2NH; (☐) – RNH_2; (×) – R_2NCH_3; (▲) – $RN(CH_3)_2$; (for experimental conditions see Table 14).



Scheme 5.

$$3MMA \rightarrow TMA + 2NH_3 \tag{6}$$

$$2DMA \rightarrow TMA + MMA \tag{7}$$

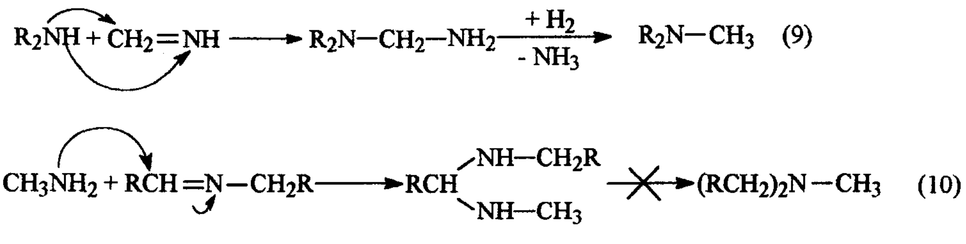
$$MMA + DMA \rightarrow TMA + NH_3 \tag{8}$$

Recent experiments have shown that there is a rapid dismutation of DMA over the nickel catalyst, therefore apparently, MMA or/and DMA are the methylating agents [52].

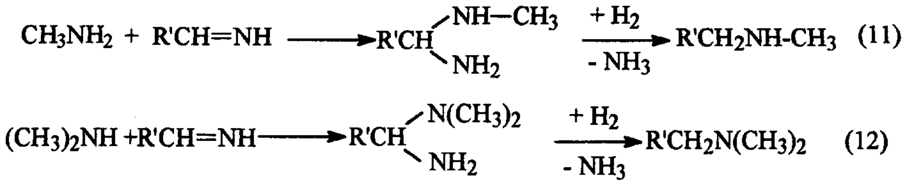
The comparisons between the rates of formation or disappearance of light amines and the rates of formation of methylated fatty amines and the studies of direct *N*-methylation reactions of dodecylnitrile with MMA or DMA [52] gave the following trends:

(i) We assume that methyldidodecylamine is formed from methylimine (originating from the catalytic dehydrogenation of MMA) and didodecylamine (reaction 9), rather than from the reaction of MMA with the secondary imine (reaction 10) (Scheme 6).

(ii) However, owing to differences in the reactivity of fatty imines it could also be (see Figs. 4 and 5) that the methylation of primary amine occurs via the reactions (11 and 12), (Scheme 7).



Scheme 6.



$$CH_3NH_2 + R'CH{=}NH \longrightarrow R'CH\begin{matrix}\nearrow NH{-}CH_3\\ \searrow NH_2\end{matrix} \xrightarrow[-NH_3]{+H_2} R'CH_2NH{-}CH_3 \quad (11)$$

$$(CH_3)_2NH + R'CH{=}NH \longrightarrow R'CH\begin{matrix}\nearrow N(CH_3)_2\\ \searrow NH_2\end{matrix} \xrightarrow[-NH_3]{+H_2} R'CH_2N(CH_3)_2 \quad (12)$$

Scheme 7.

(iii) Intermediate fatty imines would be methylated with MMA or DMA and these results could explain the differences of reactivity and selectivity observed in our experiments.

(iv) Moreover, we did not observe the direct formation of methyldidodecylamine when we studied the reaction between didodecylamine and monomethylamine. These observations would show and confirm that HMTA is mainly converted into light imines rather than light amines.

7. Conclusion

Unsymmetric alkyl amines R_2NR', and specially RNR'_2, in which R′ is a short-chain hydrocarbon can be prepared from acids, esters or nitriles and alcohols (R′OH) over promoted copper–chromite catalysts.

The selectivity and the yield of the reaction depend on the competition between two steps: (i) methylation with light alcohols (and activation of these reagents) and (ii) condensation leading first to dialkylamine. The control of the surface distribution of acid sites and metallic sites is essential for the preparation of RNR'_2 compounds. Moreover, the stability of the catalysts in the presence of water or ammonia is improved by the alkaline promoters when they are well dispersed in the copper–chromite structure.

The direct synthesis of R_2NR' is more difficult because the condensation reaction forming R_2NH compared to the methylation step on copper catalysts is not fast enough.

The total reaction rates increase if promoted nickel catalysts instead of copper–chromites are used. The selectivity is practically the same. However, over nickel catalysts we noticed a catalyst deactivation and an inhibiting effect of light alcohols (e.g. methanol).

Finally, when hexamethylenetetramine replaced methanol over nickel catalysts, it was possible, by changing just the experimental conditions, to obtain selectively either methyldidodecylamine or dimethyldodecylamine. HMTA is catalytically transformed into light amines (monomethylamine and dimethylamine) which are the actual methylating agents. The rates of formation of R_2NH and selective decomposition of HMTA can be controlled so as to obtain methyldialkylamine. Moreover, it seems that the mechanism of formation of such compounds involve mainly methylimine, while the methylation of primary amines would be produced by fatty imines and mono or dimethylamine.

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