Synthesis of dimethylethylamine from ethylamine and methanol over copper catalysts

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Abstract

The synthesis of dimethylethylamine (DMEA) from monoethylamine (MEA) and methanol was carried out in the presence of a copper chromite type catalyst. A DMEA yield of 70% was obtained under standard experimental conditions, the main by-product being diethylmethylamine. A slight increase of the basicity without any change in the metallic character of the catalyst can enhance to 85% of the DMEA formation. Indeed with such a catalyst modification, the rate of the determining steps was changed. By specific experiments involving the reactivity of intermediates it is demonstrated that the rate of the MEA condensation decreased compared to that of the MEA methylation. Moreover we show that the mechanism of the second methylation step which was different from that of the first methylation could involve an intermediate formation of an amide (MEFA) or of the surface aminoalkoxide. This step depends also on the bifunctional character of the modified copper chromite catalyst.

Keywords: Dimethylethylamine synthesis; Ethylamine reaction with methanol; Copper or copper chromite catalysts; Alkaline or alkaline–earth modifiers

1. Introduction

The synthesis of substituted light amines is performed by a heterogeneous catalysis process and from alcohol, ammonia and/or monosubstituted amine [1–4]. The applications of these amines are important in chemistry and pharmaceutic industry.

This type of process requires the formulation of a multifunctional catalyst which at a first approximation presents (i) acidic properties (activation, amine adsorption, dehydration,...) and (ii) a hydro–dehydrogenating function (methanol dehydrogenation, hydrogenation of imine and enamine intermediates).

It is well-known that copper catalysts are selective in the dehydrogenation of esters [5–7], in the hydrolysis of nitrile [8], in the selective hydrogenation of nitrile [9] or in alcohol amination [10]. The catalyst systems such as copper chromite are often used for the preparation of substituted amines. These solids, however, are very sensitive to the presence of water [11] and ammonia (formation of copper nitrides [12]). Moreover, the catalysts promoted by alkaline or alkaline–earth species are more stable than the unpromoted CuCr. For example, barium impregnated on copper chromite increases the stability of the active $CuCrO_2$ phase [13]. Furthermore, the presence of barium or calcium on

copper chromite catalysts influences strongly the selectivity to the methylation of amines: N-alkylation/N-methylation.

In our laboratory, we showed that copper chromite doped with barium, calcium or manganese can lead selectively to dimethyldodecylamine from lauronitrile, ammonia, hydrogen and methanol but not to methyldidodecylamine [14].

Among light amines, the dimethylethylamine (DMEA) is a quite important product i.e. as catalyst in polymerization processes. DMEA can be prepared from the reaction of ethanol with dimethylamine but another way consists of the reaction of methanol with monoethylamine;

$$CH_3CH_2NH_2 + 2CH_3OH$$

$$\xrightarrow{H_2} CH_3CH_2N(CH_3)_2 + 2H_2O$$
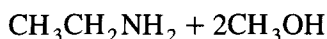
Therefore, we report, in this paper on the properties of promoted copper for the main and the side reactions and we propose a reaction scheme of monoethylamine transformation.

2. Experimental

2.1. Catalytic test

The reaction was studied in a dynamic fixed bed reactor under hydrogen pressure (1.0 MPa) at 210°C. The molar ratio MeOH/MEA was 8.2, the ratio (MeOH + MEA)/$H_2 \approx 0.85$ (where MEA: monoethylamine or ethylamine) and the catalyst weight ≈ 5 g (particle size 1.2–1.6 mm).

The reaction products were analyzed by a gas chromatograph equipped with a SGE BP1 column (L: 25 m; ID: 0.3 mm; thickness of film: 5 μm). Each catalyst was characterized by its activity and selectivity under standard conditions. The activity was obtained from the reagent conversion, the selectivity being expressed as follows;

• The first calculation refers only to eth-

ylamine (MEA) and to products resulting from the conversion of MEA (C distribution):

$$S_i(\%) = \frac{P_i}{\Sigma MEA \rightarrow P_i} \times 100.$$

• The second refers to all the products formed during the reaction (N distribution):

$$S_i(\%) = \frac{P_i}{\Sigma P_i} \times 100.$$

2.2. Catalysts

The catalyst used in this study was a copper chromite doped with barium (YP1). The other solids were prepared from that catalyst by impregnation with alkaline or alkaline–earth salts from Prolabo (LiNO₃, NaOH, KOH, KNO₃, Ca(NO₃)₂, Ba(NO₃)₂). After impregnation, the catalysts were dried in a sand-bath (120°C), and then calcinated at 350°C for 4 h under a dry air stream.

3. Results

3.1. Monoethylamine methylation in the presence of modified copper chromites

3.1.1. Reference catalyst (YP1)

The aim of this work was to obtain selectively dimethylethylamine (DMEA) from monoethylamine (MEA) and methanol (MeOH).

First, we determined the activity and the selectivity of the reference catalyst (YP1).

The results presented in Table 1 show that at 230°C, we can obtain selectively DMEA (about 70%) at complete conversion of MEA. However, at this temperature, there is a significant formation of trimethylamine (TMA). Fig. 1, which presents the change of the activity and the selectivity as function of contact time, shows clearly that methylethylamine (EMA) was the primary compound of the reaction and that the secondary product was DMEA (methylation of EMA).

For the alkylated products (condensation and methylation of MEA), diethylamine (DEA) was initially formed at low rate and the diethylmethylamine (DEMA) resulted from the methylation of DEA. A small amount of dimethylformamide (DEFA) could also be observed. All these results can be described by the reaction scheme shown in Scheme 1.

3.1.2. Effect of the addition of alkaline or alkaline–earth elements

Generally, the addition of alkaline or alkaline–earth elements to a copper chromite catalyst and the neutralization of the acid sites on the surface favor the production of primary and secondary amines due to the limitation of the condensation reactions (tertiary amine). Moreover, the presence of an alkaline–earth agent, like barium, stabilizes the active phase ($CuCrO_2$) and leads to a more stable catalyst [12].

3.1.2.1. Comparison of the effects of various alkaline or alkaline–earth elements. The YP1 catalyst was impregnated with alkaline (Li, Na, K, Cs) and alkaline–earth (Ca, Ba) elements. The catalytic properties of these solids are reported in Table 2.

The addition of an alkaline (with the exception of cesium) improved the selectivity to DMEA. With regard to the activity, it can be noticed that the conversion of MEA increased when the size of the alkaline element decreased (with the same cesium exception). On the other hand, the smaller the alkaline element, the more
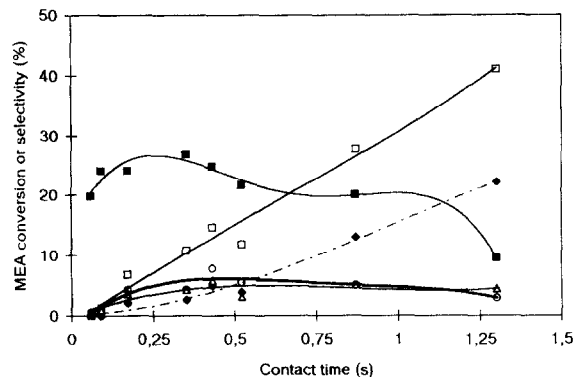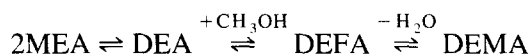

Fig. 1. N-Methylation of monoethylamine in the presence of a YP1 catalyst. Effect of the contact time: T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g. Conversion of ethylamine to: dimethylethylamine DMEA ($\square$), diethylmethylamine DEMA ($\blacklozenge$), methylethylamine EMA ($\blacksquare$), diethylamine DEA ($\bigcirc$), diethylformamide DEFA ($\triangle$).

significant was the formation of TMA. Indeed, it can be seen that a CuCr catalyst with lithium led to a DMEA selectivity of 83% whereas the one doped with cesium was less active and less selective to DMEA. It seems that the rate of the secondary methylation was much slower than the one observed over the unpromoted solid since we obtained a EMA selectivity of 60%. Moreover, there was an important proportion of DEFA (17%) while on the other catalysts there was 5% less selectivity to DEFA (DEMA was the main secondary compound). Apparently DEMA could be formed from DEFA,

$$2MEA \rightleftharpoons DEA \underset{\overset{+CH_3OH}{\rightleftharpoons}}{} DEFA \underset{\overset{-H_2O}{\rightleftharpoons}}{} DEMA$$

A similar trend was obtained with catalysts doped with alkaline–earth elements. Indeed, by

Table 1
N-Methylation of monoethylamine in the presence of a YP1 catalyst [a]

Time (h)	T (°C)	Conversion(%) MEA	Selectivity (except TMA) (%) [b]				TMA (%)
			EMA	DMEA	DEA	DEMA	
32	210	89.0	13.0	61.0	2.4	23.8	6.3
37	230	100	0.1	68.0	—	31.7	23.6
44	190	36.0	64.3	11.8	20.1	3.7	—

[a] Effect of the temperature: P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s^*, 1.3 s. (T_s^*: contact time).
[b] Selectivity to product i in relation to transformed ethylamine: $S_i(\%) = (n_i/(n_{MEA})conv) \times 100$.

$$CH_3CH_2NH_2 \underset{}{\overset{CH_3OH}{\rightleftarrows}} CH_3CH_2NHCH_3 \underset{}{\overset{CH_3OH/\,-H_2O}{\rightleftarrows}} CH_3CH_2N(CH_3)_2$$

MEA   EMA   DMEA

$$2\,CH_3CH_2NH_2 \underset{}{\overset{-NH_3}{\rightleftarrows}} (CH_3CH_2)_2NH \underset{}{\overset{CH_3OH/-H_2O}{\rightleftarrows}} (CH_3CH_2)_2NCH_3$$

MEA   DEA   DEMA

and/or

$$(C_2H_5)_2NH + (CH_3OH \longrightarrow H-\underset{\underset{O}{\|}}{C}-H) \longrightarrow H-\underset{\underset{O}{\|}}{C}-N\overset{C_2H_5}{\underset{C_2H_5}{<}} \underset{}{\overset{H_2,-H_2O}{\rightleftarrows}} \underset{C_2H_5}{\overset{C_2H_5}{>}}N-CH_3$$

DEA   MeOH   DEFA   DEMA

$$(CH_3CH_2)_2NH + CH_3CH_2NH_2 \rightleftarrows (CH_3CH_2)_3N + NH_3$$

DEA   MEA   TEA

$$CH_3OH + NH_3 \underset{}{\overset{-H_2O}{\rightleftarrows}} CH_3NH_2 \underset{}{\overset{CH_3OH/-H_2O}{\rightleftarrows}} (CH_3)_2NH \underset{}{\overset{CH_3OH/-H_2O}{\rightleftarrows}} (CH_3)_3N$$

MeOH   MMA   DMA   TMA
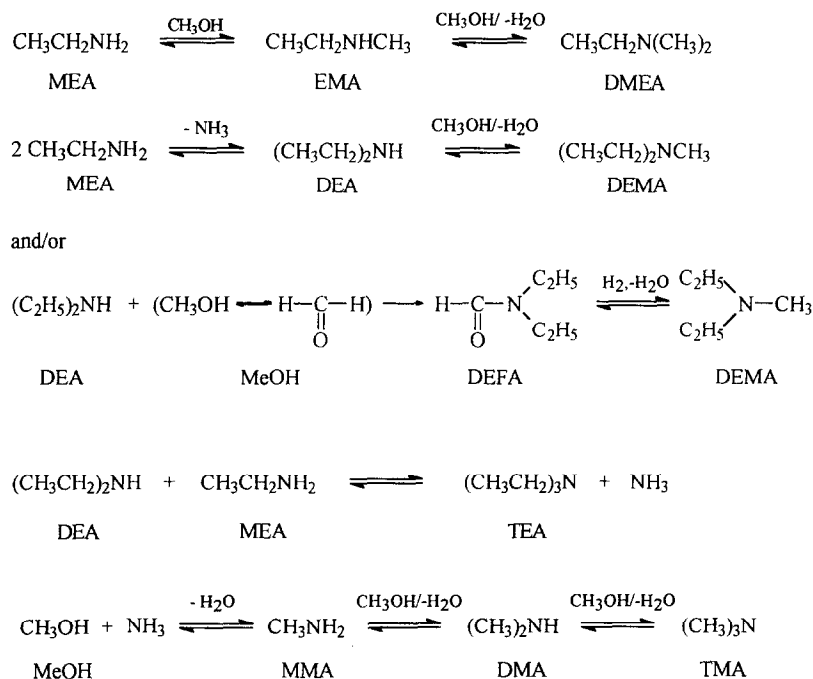
Scheme 1.

adding calcium, a catalyst, more selective to DMEA and TMA, was obtained.

3.1.2.2. Effect of lithium or of potassium content.

Several catalysts impregnated with different amounts of lithium (Fig. 2) or potassium (Fig. 3) have been used for the methylation of MEA under standard conditions. It can be noticed that there is an optimum amount of lithium (0.1 to 0.3%) or of potassium (0.5 to 1.5%) for obtaining the highest selectivity to DMEA. Actually, these amounts correspond roughly to those of the atomic content of the additive for which a maximum selectivity (83%) at total

Table 2
N-Methylation of the monoethylamine [a]

	Additive		Conversion MEA (%)	Selectivity (except TMA) (%)					TMA (%)
	weight (%)	mol ($\times 10^{-3}$)		EMA	DMEA	DEA	DEMA	DEFA	
Li [b]	0.22	3.46	85	0	83.0	0	16.7	0	37.0
Na	0.82	3.93	78	1.4	72.5	0	23.2	2.9	23.0
K [b]	1.25	3.87	100	0.2	83.4	0	15.6	0.7	9.0
Cs	—	—	69	59	22.0	1.3	1.0	17.0	0
Ca [b]	1.38	3.74	75	3.8	77.0	0	15.4	3.8	39.0
Ba [b]	3.81	3.05	79	6.6	52.5	1.6	34.1	5.2	11
YP1	—	—	88	13	61.0	2.4	23.8	—	6.3

[a] Effect of alkaline or alkaline–earth additive. Experimental conditions – Reaction time 7 to 9 h; T, 210°C; P_{H2}, 1.0 MPa.
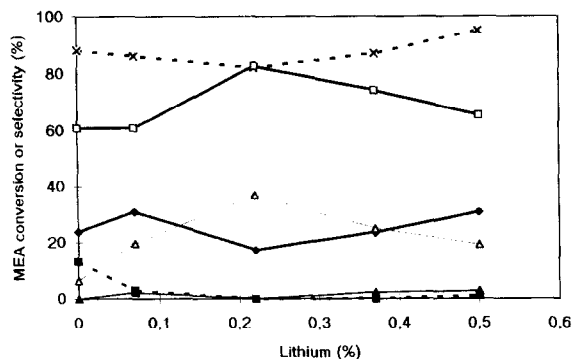[b] Precursor salts NO_3^-.

Fig. 2. Methylation of monoethylamine in the presence of catalyst Li* YP1. Effect of the lithium content: T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s. Dimethylethylamine DMEA (□), diethylmethylamine DEMA (♦), methylethylamine EMA (■), diethylformamide DEFA (▲), trimethylamine TMA (△) and MEA conversion (×).
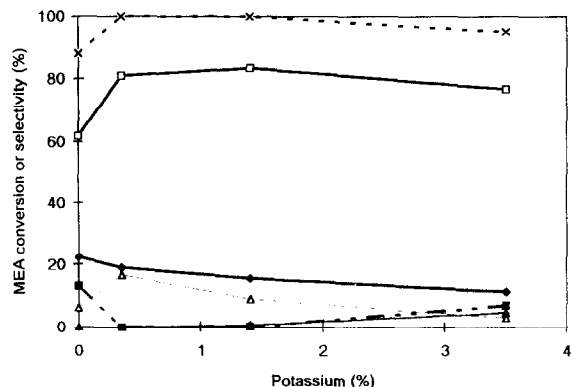

Fig. 3. N-Methylation of monoethylamine in the presence of a KYP1 catalyst. Effect of the potassium content: T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s. Dimethylethylamine DMEA (□), diethylmethylamine DEMA (♦), methylethylamine EMA (■), diethylformamide DEFA (▲), trimethylamine TMA (△) and MEA conversion (×).

conversion of the reactant can be observed. However, the activity of the potassium promoted catalyst seems higher than that obtained after the addition of lithium. Moreover, TMA selectivity is lower when potassium is used as a promoter and decreases slightly when the amount of this element is increased.

We believe, in agreement with works concerning the preparation of electrodes [15], that the lithium can be easily inserted in a copper chromite system. It can thus modify the hydro–dehydrogenating properties of copper so that the TMA formation can be increased.

3.1.2.3. Influence of the potassium precursor. We have compared catalysts KYP1 impregnated either with KNO_3 (noted *) or with KOH. The results, listed in Table 3, show that the nitrate precursor decreases the activity and the selectiv-

ity of DMEA. We can suppose that the modification of the acidity of the support depends on the precursor used. However, the hydro–dehydrogenating characteristics are also improved by potassium hydroxide. If the acid properties depend on the potassium precursor, it is surprising that the hydrogenative ability of the catalyst varies with the change of the potassium precursor, unless the dispersion of the copper phase is modified.

3.1.3. Influence of temperature or pressure

3.1.3.1. Effect of the reaction temperature – Stability of catalysts. The change of the properties of the 2.5Li* YP1 and 3.5KYP1 catalysts with the temperature gives the information shown in Tables 4 and 5. It can be noticed that

Table 3
N-Methylation of monoethylamine in the presence of a 2KYP1 catalyst [a]

Precursor	Conversion MEA (%)	Selectivity (except TMA) (%)				TMA (%)
		EMA	DMEA	DEA	DEMA	
'OH' 2KYP1	100	0.2	83.4	0	15.6	9.0
'NO₃' 2K* YP1	91	23.7	61.4	1.7	13.2	2.8

[a] Effect of the potassium precursor: T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s.

Table 4
N-Methylation of monoethylamine in the presence of catalyst 3.5KYP1 [a]

Reaction time (h)	T (°C)	Conversion MEA (%)	Selectivity (except TMA) (%)					TMA (%)
			EMA	DMEA	DEA	DEMA	DEFA	
14	210	98	1.2	72.7	0	26.1	0	12.6
41	210	79	2.2	71.2	0	24.8	1.7	23
24	230	100	0	90.1	0	9.9	0	32.5
36	190	56	41.6	32.1	10.6	10.9	4.7	0

[a] Effect of the reaction temperature: P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s.

the DMEA selectivity increases with the temperature whatever the additive (K or Li). For temperatures between 230°C and 250°C, the selectivity is around 90% when there is total conversion of MEA. However, the amount of TMA formed and the stability of the catalyst depend very much on the additive. Indeed, the selectivity to TMA, which is favored by the temperature, is also much more significant with a lithium additive for the reason already given. Moreover, it can be observed that the activity of lithium promoted catalysts decreases after short reaction time (compare conversions after 14 h and 41 h at 210°C in Table 4) whereas there is no deactivation with a potassium additive (com-

pare conversions after 33 h and 106 h at 220°C in Table 5).

3.1.3.2. Effect of the total pressure. The main reaction was studied for a pressure between 4 and 15 bar (hydrogen). Table 6 gives the results. It is obvious that the selectivity to DMEA is improved by the pressure. However, there is an optimum pressure of 10 bar for which there is a maximum selectivity to DMEA. For lower pressures, it can be seen that the methylation step is not complete whereas the condensation of MEA to DEA and the formation of DEMA increase for higher pressures (this result is in agreement with the rules of thermodynamics). Thus, the

Table 5
N-Methylation of monoethylamine in the presence of a 3.5KYP1 catalyst [a]

Reaction time (h)	T (°C)	Conversion MEA (%)	Selectivity (except TMA) (%)						EtOH + TMA (%) [b]
			EMA	DMEA	DEA	DEMA	DEFA	TEA	
33	220	82	41.4	44.8	1.3	2.2	10.2	0	0
106	220	84.2	41.6	42.9	1.5	2.8	11.2	0	0
21	230	100	2.2	78.1	0	3.0	1.9	5.3	7.0
26	250	100	0	89.6	0	3.4	1.5	5.5	21.4

[a] Effect of the temperature: P_{H2}, 10 MPa; catalyst weight, 5 g; T_s, 1.3 s.
[b] During these experiments, we observed the formation of both TMA and EtOH (the main product).

Table 6
N-Methylation of monoethylamine in the presence of a 2KYP1 catalyst [a]

Total pressure (MPa)	Time (h)	Conversion MEA (%)	Selectivity (except TMA) (%)					TMA (%)
			EMA	DMEA	DEA	DEMA	DEFA	
1.0	4.5	97	0	88.3	0	11.5	0.2	9.8
1.0	17.5	97	0.6	87.8	0	10.9	0.6	8.6
1.5	8.5	95	1.0	85.9	0	12.9	0.2	11.2
0.4	11.5	95	5.9	75.8	0	10.4	7.8	4.2

[a] Effect of the hydrogen pressure: T, 210°C; catalyst weight, 5 g; T_s, 1.3 s.

Table 7
Disproportionation of monoethylamine in the presence of a 2KYP1 catalyst [a]

Catalyst	Conversion MEA (%)	Selectivity (%)					
		EMA	DMEA	DEA	DEMA	TMA	TEA
2KYP1	78.2	—	—	71.7	—	—	28.3

[a] Reactivity of ethylamine in the absence of methanol: T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g, T_s, 1.3 s.

increase of the partial hydrogen pressure involves (i) a partial modification of surface coverage of reactants and products and (ii) the maintaining of the metallic surface necessary for the hydrogenation and the dehydrogenation steps [12].

3.2. Reactivity of monoethylamine or other intermediates

In order to determine the main steps of the formation of different products, we studied, under identical experimental conditions with a YP1 catalyst, the reactivity of the main compounds with or without reagents (MEA, MeOH).
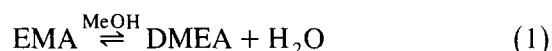
3.2.1. Reactivity of monoethylamine (in the absence of methanol)

The reactivity of this amine under standard conditions was studied replacing methanol with n-heptane (inert solvent). In agreement with the reaction scheme, ethylamine was transformed mainly, first into DEA and then into TEA (Table 7). Moreover, it can be noticed that the rate

of the reaction of MEA with the corresponding imine to form the DEA was lower than the rate of the reaction of MEA with methanol.

3.2.2. Reactivity of methylethylamine (EMA), diethylamine (DEA) and dimethylethylamine (DMEA) in the presence of MeOH and H_2

- Under similar experimental conditions, EMA was methylated rapidly by methanol into DMEA (95%) plus a small amount of DEMA (Table 8). The following reactions could explain the formation of these products;

$$EMA \overset{MeOH}{\rightleftharpoons} DMEA + H_2O \qquad (1)$$

$$DMEA \overset{MeOH}{\rightleftharpoons} EtOH + DMA \qquad (2)$$

$$EMA + EtOH \rightleftharpoons DEMA + H_2O \qquad (3)$$

$$2MEA \rightleftharpoons DEMA + MMA \qquad (4)$$

From Eq. (4), it can deduced that the N–CH_3 bond could be formed before the second N–Et bond.

- On the other hand, diethylamine was easily methylated by methanol (selectivity to DEMA: 95%). However, DEMA can be transformed into DMEA (Table 8). Moreover, the comparison between the results obtained from EMA and from DEA also shows that DEA is much more reactive than MEA. Besides Eq. (1) (Eq. (5) below), Eqs. (6) and (7) could depict the transformation of DEA;

$$EMA + MeOH \rightleftharpoons DMEA + H_2O \qquad (5)$$

$$DEA + MeOH \rightleftharpoons DEMA + H_2O \qquad (6)$$

$$DEA + MeOH \rightleftharpoons EMA + EtOH \qquad (7)$$

Table 8
Reactivity of various intermediates with methanol over a YP1 catalyst [a]

Reagent	Time (h)	Conversion MEA (%)	Selectivity (%)						TMA + EtOH (%)	DMA (%)
			EMA	DMEA	DEA	DEMA	TEA	DEFA		
EMA	8	100	—	95.1	—	4.9	—	—	5.0	4.9
DEA [b]	8	100	—	4.7	—	95.3	—	—	2.5	2.2
DMEA	10	6.8	—	—	—	—	—	—	0	100
	45	5.4	—	—	—	—	—	—	33.1 [c]	66.9

[a] T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s.
[b] Catalyst weight, 1 g.
[c] Ethanol.

• Experiments starting from DMEA (Table 8) show that this compound is much less reactive and is converted only into DMA and ethanol. It is rather difficult to explain the formation of these products. Nevertheless, (1) a modification of the catalytic properties with reaction time could be noticed; (2) if the formation of dimethylamine and ethanol is obtained, the formation of TMA or of a hydrocarbon like ethane or methane, is not. Therefore, we suppose that (i) some of the methanol is dehydrated into dimethylether (Eq. (9)); and (ii) the water issued from the dehydration step reacting with DMEA (Eq. (8)) forms DMA and EtOH, part of this alcohol being also dehydrated, especially in the presence of the fresh catalyst.

$$H_2O + DMEA \rightarrow DMA + EtOH \qquad (8)$$

$$2CH_3OH \rightleftharpoons (CH_3)_2O + H_2O \qquad (9)$$
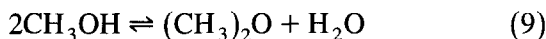
These results demonstrate the role of methanol during the synthesis of DMEA. On the one hand, it acts as a methylating agent of ethylamine and on the other it inhibits strongly the alkylation reactions: MEA disproportionation into DEA and TEA.
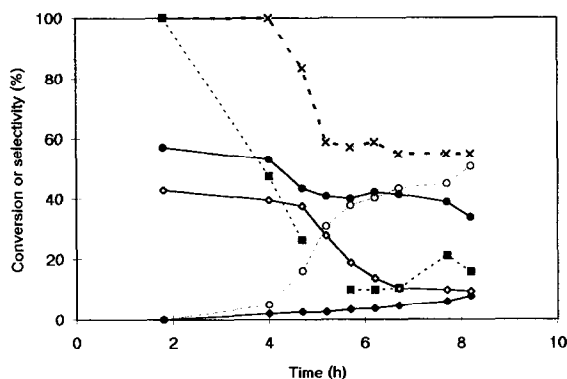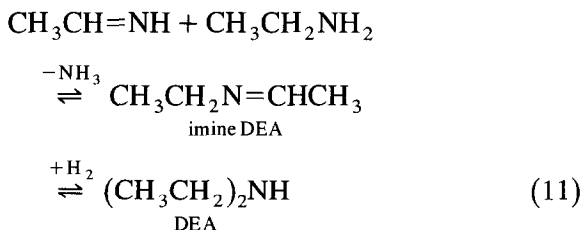

Fig. 4. Reaction between monoethylamine and methylethylamine over the 2.5Li* YP1 catalyst. T, 210°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s. Methylethylamine EMA conversion (■), ethylamine MEA conversion (×). Selectivity to diethylamine DEA (○), imine of DEA (●), diethylmethylamine DEMA (◆), enamine of DEMA (◇).

3.2.3. Reactions between ethylamine (MEA) and methylethylamine (EMA)

In the absence of methanol (replaced by n-heptane), Fig. 4 shows that initially these two reactants are transformed rapidly. Surprisingly, we observe:

(1) The imine, $CH_3-CH_2-N=CH-CH_3$ is the main product. This compound is the intermediate in the formation of the DEA (Eqs. (10) and (11),

$$CH_3CH_2NH_2 \rightleftharpoons CH_3CH=NH + H_2 \qquad (10)$$

$$CH_3CH=NH + CH_3CH_2NH_2$$

$$\overset{-NH_3}{\rightleftharpoons} \underset{\text{imine DEA}}{CH_3CH_2N=CHCH_3}$$

$$\overset{+H_2}{\rightleftharpoons} \underset{\text{DEA}}{(CH_3CH_2)_2NH} \qquad (11)$$

(2) The enamine, $CH_3-CH_2-(CH_3)-N-CH=CH_2$; compound formed from the reaction of MEA with ethylenimine (Eq. (12)) which is further hydrogenated into DMEA.

$$(12)$$
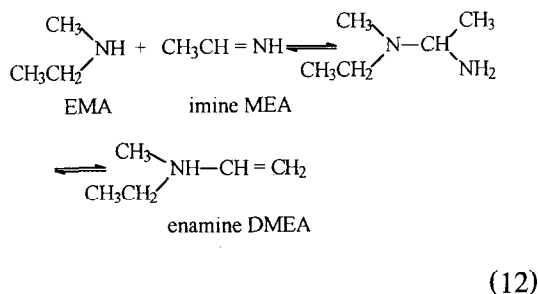
The hydrogenation steps are the rate limiting steps over the fresh catalyst. After two hour experiment, we observed a dramatic decrease of the activity, specially of the MEA conversion and the disappearance of the intermediates. Furthermore, DEMA and DEA which are the main products, are formed. These results show that the adsorption properties of the catalysts vary greatly during the reaction since ethylamine is mainly adsorbed and leads to DEA. We suppose that these significant modifications could be due

Table 9
N-Methylation of monoethylamine

Catalyst	Time (h)	Conv. MEA (%)	Selectivity (%) (except TMA)					TMA (%)
			EMA	DMEA	DEA	DEMA	DEFA	
Li⁺ 0.2%	24	100	0	90.1	0	9.9	0	32.5
K 3.5%	16.5	99	0	94.2	0	5.8	–	7.5
YP1	37	100	0.1	68.1	0	31.7	–	23.6

Comparison of the catalytics properties of a YP1 catalyst modified with Li or K.
T, 230°C; P_{H2}, 1.0 MPa; catalyst weight, 5 g; T_s, 1.3 s.

to the polymerization of reaction intermediates such as imine or enamine. The polymers could remain on the catalyst surface and modify the nature and the number of active sites. In previous works, we have already observed that these secondary reactions can modify the catalyst surface [16].

This result also demonstrates that methanol inhibits strongly the reactions since they are much less significant in the presence of methanol.

4. Discussion

In the first part of our work, we examined the properties of a copper chromite catalyst for the synthesis of dimethylethylamine (DMEA) from monoethylamine (MEA) and methanol (MeOH).

Under our experimental conditions, this catalyst was rather selective (70%) at total conversion of the reactant. Moreover, in this study, we showed that methylethylamine was the primary product of the reaction, whereas dimethylethylamine was a secondary compound formed from EMA. The other products, issued from condensation and methylation reactions, were DMEA, DEFA and TEA. Furthermore, we observed the formation of mono-, di- and trimethylamine (TMA).
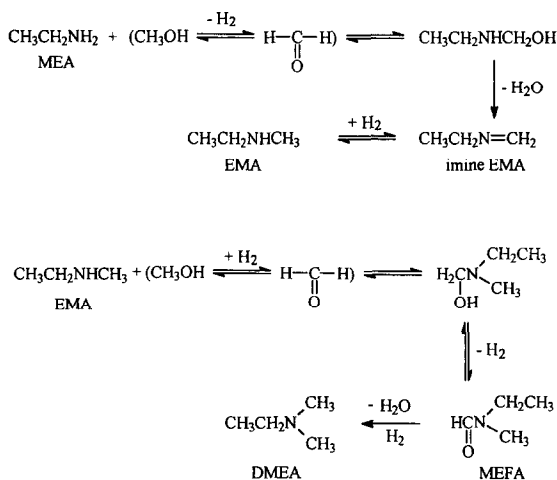
On the other hand, we investigated the increase of the DMEA selectivity and the decrease in the formation of DEA and DEMA. As these amines result from a condensation reaction of MEA which requires the presence of acid sites on the surface of the catalyst, adding alkaline or alkaline–earth elements decreases the reaction rate. Here, the addition of a small amount of KOH (0.5 to 2%) decreased the quantity of DEMA formed and increased the selectivity to DMEA without changing the activity (Table 9). A similar result was obtained by adding lithium (0.2–0.3%). However, the TMA selectivity was much more significant. Therefore, it seems that the hydro–dehydrogenating properties of copper are enhanced in the presence of lithium because methylamines are formed from the amination of intermediate species resulting from methanol dehydrogenation.

We also studied the effect of the other (alkaline or alkaline–earth) additives and showed that these additives also changed the properties of the reference catalyst. However there was more EMA, DEMA and DEFA formed. The TMA selectivity was reduced when the solid was doped with cesium or barium. This means that the second N-methylation decreased as a result of a decrease of the C–O hydrogenolysis properties when the size of the alkaline or the alkaline–earth ion increased. Indeed, the mechanism of the second N-methylation step for the formation of DMEA or DEMA via the intermediates MEFA and DEFA was different from the one involved in the first N-methylation step.

As there was no hydrogen linked to the carbon of the CO bond the formation of DMEA and DEMA required an adsorption step of

MEFA or DEFA via an alkoxide species and a concerted elimination hydrogenation reaction,

$$CH_3CH_2NH_2 + (CH_3OH \xrightleftharpoons{-H_2} H-\underset{\underset{O}{\|}}{C}-H) \rightleftharpoons CH_3CH_2NHCH_2OH$$
MEA

$$CH_3CH_2NHCH_3 \xleftrightarrow{+H_2} CH_3CH_2N{=}CH_2 \quad \Big\uparrow {-H_2O}$$
EMA   imine EMA

$$CH_3CH_2NHCH_3 + (CH_3OH \xrightleftharpoons{+H_2} H-\underset{\underset{O}{\|}}{C}-H) \rightleftharpoons H_2CN\overset{CH_2CH_3}{\underset{OH}{\diagdown CH_3}}$$
EMA

$$\Big\updownarrow {-H_2}$$

$$CH_3CH_2N\overset{CH_3}{\underset{CH_3}{\diagdown}} \xleftarrow[H_2]{-H_2O} HCN\overset{CH_2CH_3}{\underset{\underset{O}{\|}}{\diagdown CH_3}}$$
DMEA   MEFA

On the other hand, the selectivity to DMEA increased significantly with the temperature. There was also a substantial formation of ethanol and TMA via

$$DMEA \diagup\diagdown \begin{matrix} EtOH + TMA \\ + CH_3OH \;\Big\updownarrow\; + H_2O \\ EtOH + DMA \end{matrix}$$
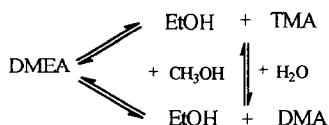
In a second part, in order to corroborate the main steps of the synthesis of dimethylethylamine and the main by-products, we studied the reactivity of some intermediates and products.

In the absence of methanol, ethylamine is transformed mainly into diethylamine (DEA), the deactivation of the catalyst being very fast due to an increase of ammonia formation. Baiker and Kijenski showed, for instance, that part of the copper was transformed into copper nitride during the amination of alcohols [12]. In the presence of methanol, the ethylamine surface coverage is lower and one observes a decrease of the DEA formation. Methanol acts as an inhibitor in the DEA synthesis and as a promotor of the catalyst duration.

The methylation rate of diethylamine with methanol is more significant than that of meth-

ylethylamine (EMA). This result was expected on account of the change of amines reactivity with the N-substitution. On the other hand, DMEA does not react with methanol or DEMA and there is no formation of TMA or TEA.

In the absence of methanol, EMA easily reacts with MEA and an enamine intermediate in the formation of DEMA is obtained. Indeed, owing to a catalyst modification during the reaction this amine is not formed, in the presence of methanol, the formation of DEMA compared to that of the methylation of EMA is more reduced.

Briefly, this part of our work on the reactivity of intermediate or of by-products shows the reasons for the necessity of using an excess of methanol for the synthesis of DMEA from [MEA, MeOH, H_2].

5. Conclusion

In summary, from all this study the reaction scheme of the transformation of ethylamine to the main product DMEA and by-products as shown in Scheme 2 was established.

From a kinetic point of view, steps 2 and 3
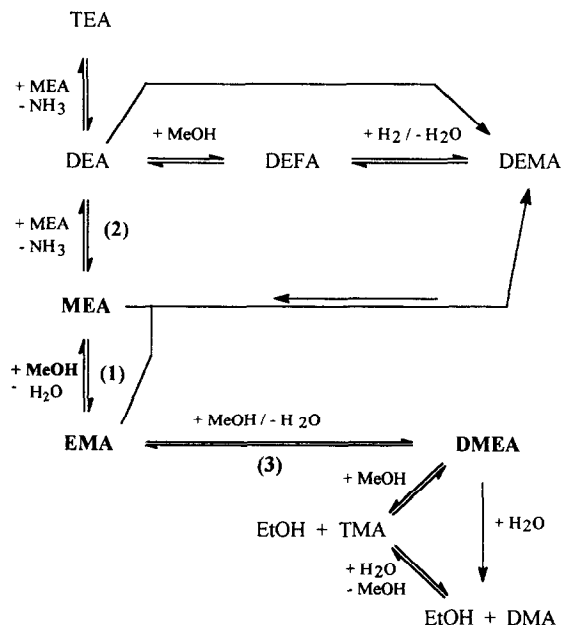
Scheme 2.

are the rate determining reactions. It follows that the DMEA selectivity is increased by modifying the acido-basicity of copper chromite used as a catalyst. In fact, the change of the catalyst basicity can decrease the MEA condensation into DEA without modification of the hydro–dehydrogenating properties of the catalyst which are necessary for the methylation of the ethylamine with methanol (steps 1 and 3).

Acknowledgements

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