

Selectivity Control in Substituted Fatty Amines Synthesis from Esters or Nitriles in the Presence of Bifunctional Catalysts

J. Barrault^{a,*}, S. Brunet^a, N. Suppo-Essayem^a, A. Piccirilli^a and C. Guimon^b

^aLaboratoire de Catalyse, URA CNRS 350, ESIP, 86022 Poitiers Cedex, France and ^bLaboratoire de Physicochimie Moléculaire, URA CNRS, 474, 64000 Pau, France

Copper chromite-type catalysts, supported by alumina or graphite and promoted with barium, were used for the one-step synthesis of tertiary fatty amines [R₂NCH₃ or RN(CH₃)₂] from ester, acid or nitrile and ammonia, methanol and hydrogen. The surface composition of the catalysts, studied by X-ray photoelectron spectroscopy and by adsorption experiments, showed that there was a correlation between selectivity and the presence of a well-dispersed CuCrO₂ phase, stabilized with barium. Moreover, the elements influencing the stability of the copper catalysts were also studied, and the promoter or/and the support increased the copper surface area and the stability of the catalyst in the presence of water or ammonia.

KEY WORDS: Amination of fatty acids, amination of fatty esters, barium, calcium, copper chromite supported catalysts, hydrogenation of nitriles, influence of promoters, influence of support, manganese, N-methylation of amines.

There are numerous methods for synthesizing fatty aliphatic amines, but only a few are being used industrially. The industrial methods include the hydrogenation of fatty nitriles and the amination of alcohols. The precursors can come from natural or petrochemical sources, but the former are being used more and more.

Hydrogenation/condensation of a nitrile often leads to a mixture of primary, secondary and tertiary amines, this reaction has been described by Von Braun *et al.*, Greenfield (2) and Volf and Pasek (3). However, with a wise choice of catalyst, the relative yield of primary amines (Co, Ni) (4,5), secondary amines (Cu) (3) or tertiary amines (Rh) (6) can be increased. Moreover, the nature of the support and the choice of a promoter play a determining role in the activity and selectivity (6–9) of the catalyst.

Amination of alcohols (particularly fatty alcohols) generally consists of a reaction between an aliphatic alcohol and an amine, such as NH₃, CH₃NH₂ or (CH₃)₂NH. This reaction is most selective with a primary amine or ammonia, but leads more readily to a tertiary amine RN(CH₃)₂ when (CH₃)₂NH is used. According to Kliger *et al.* (10) and Baiker and Kijenski (11,12), the most significant step is the dehydrogenation of the alcohol.

The catalysts are often copper-based, dispersed on a support and/or promoted and used with an excess of hydrogen. It has been shown that this excess was indispensable in preventing the deactivation of the catalyst due to the formation of nitrides and/or carbonaceous layers (11,12). These results indicate a number of key steps: (i) formation and selective transformation of imines (RCH=NH, RCH=NR'); (ii) dehydrogenation of alcohol and addition of the adsorbed carbonyl species to amines; and (iii) disproportionation of amines.

These steps control the activity and the overall selectivity of the reaction. Thus, to improve currently known processes

or to search for new ones require both a better knowledge of these reaction steps and a more detailed description of the catalysts and their active sites. In this paper, we report data obtained during the direct transformation of esters, acids or nitriles into substituted amines in the presence of supported copper chromite catalysts. The variations in selectivity were studied in relation to the composition of the catalytic surface.

EXPERIMENTAL PROCEDURES

Catalysts. The catalysts were prepared by precipitation (for monometallic catalysts) or co-precipitation (for bimetallic catalysts) of copper and chromium hydroxides in the presence of a support. Sodium carbonate was used to carry out the precipitation (80°C, pH = 7.5). The precipitates were washed, dried and then calcined in air at 350°C for 8 h.

Before X-ray photoelectron spectroscopic (XPS) characterization, the reduced samples (10 h at 350°C under H₂ flow) were stored under inert atmosphere in sealed vials, then placed in a glove-box coupled with the XPS chamber to prevent any oxidation before the analysis.

XPS. XPS analyses were performed with an SSI (Surface Science Instruments, Mountain View, CA) model 301 spectrometer with focused (diameter of the irradiated area: 600 μm) monochromatic Alk α radiation (10 kV, 10 mA) and coupled with a glove-box (≤2 ppm of O₂ and 6 ppm of H₂O in a nitrogen atmosphere), which was used for the transfer of the samples pre-reduced with hydrogen. The residual pressure inside the analysis chamber was about 5 · 10⁻⁸ Pa. The sample charging effects were minimized with a low-energy flood gun (5 eV). The calibration of the spectra was performed with the Al 2p line (74.2 eV) from an Al₂O₃ support. The spectra were recorded in the constant pass energy (50 eV) mode.

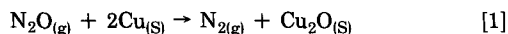
The oxidation states of the metals were determined by measuring the binding energies Cu 2_{p_{3/2}} and Cr 2_{p_{3/2}}. For chromium, the Cr 2_{p_{3/2}} spectrum of Cr₂O₃(Cr^{III}) showed a peak at about 576.5 eV (13). In CrO₃(Cr^{VI}), the binding energy was between 578 and 579 eV.

For copper species, Cu⁰ and Cu^I had a Cu 2_{p_{3/2}} line at the same position (about 932 eV). These oxidation states could be distinguished with the X-ray-induced Auger electron lines (L₃M_{4,5}M_{4,5}). These Auger line positions were, (in kinetic energy) 919 eV for Cu⁰, 916.7 eV for Cu^I and 918.2 eV for Cu^{II} (14). Thus, when Cu^{II} was not present in large amounts, Cu⁰ and Cu^I could be easily detected. Cu^{II} can be distinguished from the other two oxidation states by the position of the main photoelectron peak Cu 2_{p_{3/2}} at about 934 eV (15,16), which shows a larger width [due to multiplet splitting (17,18)] and by the presence of satellite (shake-up) bands (19–21) arising from ligand-metal electron transfer (22). The intensity of the shake-up peaks (I_{sat}), compared to that of the main (I_{mp}), is characteristic of the crystal structure and of the symmetry of cuprous oxide (23–25). So I_{sat}/I_{mp} is about 0.55 for CuO (26), a value close to the one corresponding to a

*To whom correspondence should be addressed at Laboratoire de Catalyse, URA CNRS 350, ESIP, 40 av. du Recteur Pineau, 86022 Poitiers Cedex, France.

square plane symmetry, and 0.8 for Cu-CrO₄ (25) (spinel structure).

Pulse-chromatographic N₂O titration of the copper surface area. The Cu surface area is usually determined by reactive chemisorption of nitrous oxide as a probe molecule according to the reaction:



Several techniques for monitoring the course of this reaction and the completion of the monolayer have been developed, and we used the pulse-chromatographic method (27). The preactivated catalyst is exposed to a known quantity of N₂O (pulses) at room temperature or at 353°K, and the amounts of N₂O consumed and N₂ produced are determined. In the current literature there is general agreement on the stoichiometry of the monolayer formed by dissociative adsorption, with Cu_(s): O_{ads} = 2:1. The copper surface area is calculated by using different average values of the surface atom density, based on theoretical calculations of a uniform distribution of crystallographic planes (28).

Catalytic reactions. The amination of esters or acids and the hydrogenation of nitriles were carried out in a flow fixed-bed reactor under pressure (3–8 MPa). Esters, acids, nitriles, methanol, ammonia and hydrogen were continuously fed into the reactor *via* calibrated pumps and mass flowmeters. Liquid products issued from the reactor were condensed and analyzed by off-line gas chromatography.

RESULTS AND DISCUSSION

Catalyst characterization. We compared the bulk and surface characteristics of alumina- and graphite-supported catalysts as well their adsorption properties.

The chemical composition and the main phases identified by X-ray diffraction are reported in Table 1. The spectra were obtained with the more selective catalysts. Alumina-supported samples were preactivated with hydrogen at 623°K, but the other samples were not reduced before characterization. Quite well-crystallized phases on alumina-supported catalysts were observed, i.e., CuCr₂O₄ for unpromoted catalysts and BaCrO₄ for barium-promoted catalysts. Less crystalline solids were obtained when graphite was used as support. In this case, different phases were observed, i.e., CuCrO₂ and Cu₂O, which showed that the support had a significant effect on the bulk composition of the catalyst.

The XPS characteristics, presented in Table 2, showed that the surface composition of the catalysts depended greatly on the support. For alumina-supported catalysts, a copper surface enrichment was obtained that was not modified by the addition of barium (before reduction). After reduction of the CuCr/Al₂O₃ catalyst with hydrogen at 623°K, we observed a significant change of the surface Cu/Cr ratio from 1.46 to 0.75, although the modification is less important for CuCrBa/Al₂O₃ (1.50 → 1.26). This result could indicate that barium prevents the copper sintering that generally occurs during the hydrogen treatment at high temperature. Moreover, Table 3 demonstrates that, in the presence of barium, copper oxide was not totally reduced with hydrogen at 623°K. The Auger line at 918.2 eV instead of at 918.9 eV is a strong indication of the presence of equivalent amounts of Cu^I and Cu⁰. On the other hand, the Cr 2_{p_{3/2}} lines were not modified by the presence of barium so that BaCr₂O₄ or BaCrO₄ was not formed and only Cr^{III} species could be observed after reduction (Table 2).

For CuCr-graphite catalysts, the surface copper and chromium contents are rather similar to the previous ones. The addition of barium decreases the number of copper

TABLE 1

Bulk Composition of Copper Chromium Catalysts

	CuCr/Al ₂ O ₃	CuCrBa/Al ₂ O ₃	CuCr/graphite	CuCrBa/graphite
Cu content (wt%)	5.4	5.5	5.9	5.8
Cr content (wt%)	5.6	4.3	4.1	5.0
Cu/Cr (atom)	0.8	1.05	1.18	0.95
Ba content (wt%)	0	4.4	0	1.2
X-ray diffraction (identified phases)	CuCr ₂ O ₄	BaCrO ₄	Less crystalline	CuCrO ₂ Cu ₂ O

TABLE 2

Surface Composition of CuCr(Ba) Catalysts Supported by Alumina or Graphite

Catalysts		Cu/Al or (C)	Cr/Al or (C)	Cu/Cr	Ba/Cr	Relative atomic ratio
CuCr/AlO ₃	(a) ^a	0.080	0.051	1.46	—	Cu/Cr = 1:1.2
CuCrBa/AlO ₃	(b)	0.023	0.031	0.75	—	Cu/Cr/Ba = 1:1:0.4
	(a)	0.056	0.037	1.50	0.13	
CuCr/graphite	(b)	0.024	0.019	1.26	0.15	Cu/Cr = 1:0.8
	(a)	0.087	0.070	1.26	—	
CuCrBa/graphite	(a)	0.033	0.044	0.74	0.11	Cu/Cr/Ba = 1:1:0.1

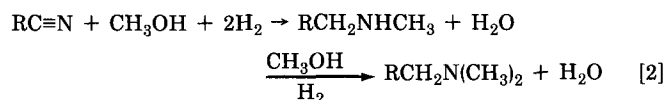
^a(a), Not reduced; (b) reduced at 623°K.

SELECTIVITY CONTROL IN SUBSTITUTED FATTY AMINES SYNTHESIS

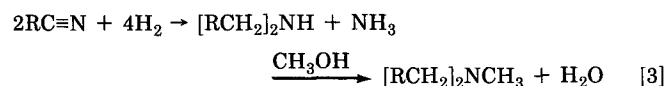
and chromium atoms, but there is a relative chromium enrichment because the Cu/Cr ratio decreases from 1.26 to 0.74. In comparison with alumina-supported catalysts, this result is quite different. Moreover the Cu^I content was higher (45%) (Table 3) and was the opposite with Cr^{VI} species, which disappear completely after addition of barium and lead only to Cr^{III} species, without any modification of the Cr 2_{p3/2} lines.

We propose that at the surface of alumina and after the reduction of the catalyst, there is formation of metallic copper (Cu⁰), chromium oxide (Cr₂O₃) and of a small amount of copper chromite (CuCrO₂), the latter species being favored by the presence of barium. Moreover, we observed that copper species are in excess before and after hydrogen reduction. Also, at the surface of graphite (without reduction with hydrogen), we observed copper oxide (CuO) and chromium oxide species (Cr₂O₃) in excess, but the main characteristic of these catalysts is the important formation of a copper chromite phase (CuCrO₂). It seems that barium has no significant effect on the nature of copper and on chromium species formed at the surface of the catalysts, and from these characterizations we have no clear evidence of the localization of this additive.

We will explore further the role of barium with regard to the presence of water and/or ammonia. When lauro-nitrile is totally transformed into dimethyldodecylamine in the presence of methanol and hydrogen, water is the main product formed:



Formation of methyldidodecylamine is accompanied by the formation of water and ammonia:

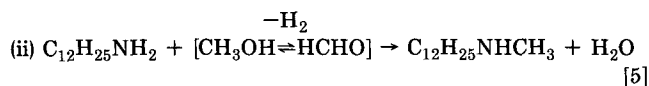
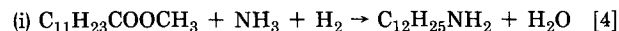


These latter two products could act like catalyst modifiers, particularly of copper catalysts (11). Therefore, we were led to examine the modification of the copper metallic surface area (N₂O decomposition) by following the addition of known amounts of water or ammonia at 623° K. These experiments were performed *in situ* in the micro-reactor used for the metallic surface area measurement.

Figure 1 gives the variations of the accessible copper surface area for CuCr(Ba)/graphite catalysts as a function of the addition of water and of ammonia (S/So, where So and S designate the copper surface area before and after, respectively, introduction of the modifier). The quantity of modifier is expressed relatively to the number of copper atoms initially accessible. The results evidenced that water has a significant inhibiting effect, even if it is more subtle, than ammonia on nonpromoted catalysts. On the other hand, after adding barium, a substantial fraction of the initial metallic surface area is conserved, even after adding significant amounts of water and ammonia. In relation to XPS characterization, barium could stabilize the CuCrO₂ chromite phase and significantly increase the stability of the catalysts.

Results obtained with CuCr(Ba) alumina-deposited catalysts are presented in Figure 2. Ammonia has a marked inhibiting effect on nonpromoted catalysts. Moreover, the addition of the promoter strongly increases the stability of the catalysts in the presence of ammonia and of water. However, contrary to graphite-supported catalysts, the addition of a promoter does not allow complete stabilization of the catalyst in the presence of ammonia, and of water in particular.

Amination of methyl dodecanoate or dodecanoic acid in the presence of alumina- or titania-supported CuCr catalysts. Table 4 shows that methyl dodecanoate is easily converted into amine in the presence of CuCr deposited on alumina or on titania, and one can observe that the difficult methylation reaction is favored by alumina. Moreover, a significant increase of *N*-dimethyldodecylamine is obtained when the reaction is carried out with a large excess of hydrogen. Due to 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 into a carbonyl compound; and (ii) a further reaction of this compound with primary amine or secondary amine *via* imine or enamine intermediates (10-12):



This hydrogen effect can be explained by the low hydrogen coverage which, under normal conditions, is not

TABLE 3

Oxidation State of Surface Copper and Chromium Species

Catalysts		Binding energy (eV)		I _{sat} I _{mp}	Cu ^{I/0}		Cu-binding energy (eV) _{Auger}	Cr ^{VI}	
		Cu ^{II}	Cu ^{-/0}		Cu total (%)	Cr total (%)			
CuCr/AlO ₃	(a) ^a	934.7	932.5	0.77	21	—	—	—	47
	(b)	—	931.9	—	100	918.9	Cu ⁰	—	ε
CuCrBa/AlO ₃	(a)	933.9	932.1	0.5	19	—	—	—	46
	(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	(a)	934.0	931.8	0.64	46	916.6	Cu ^I	—	ε

^aAs in Table 2.

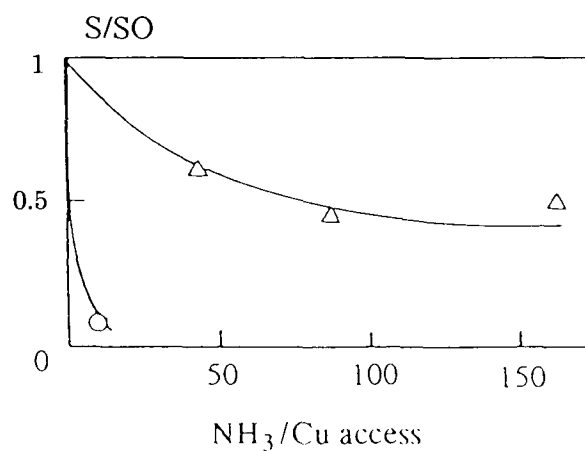
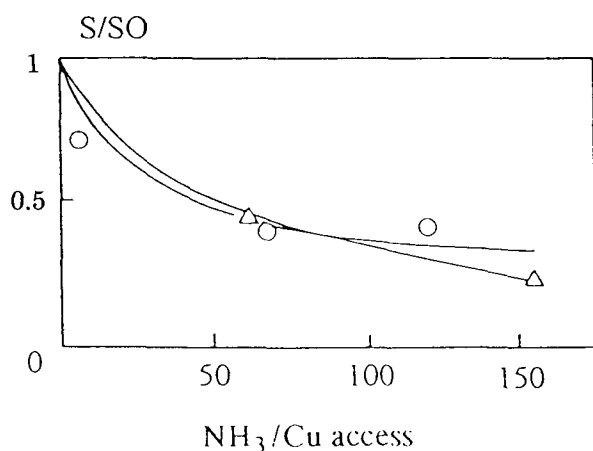
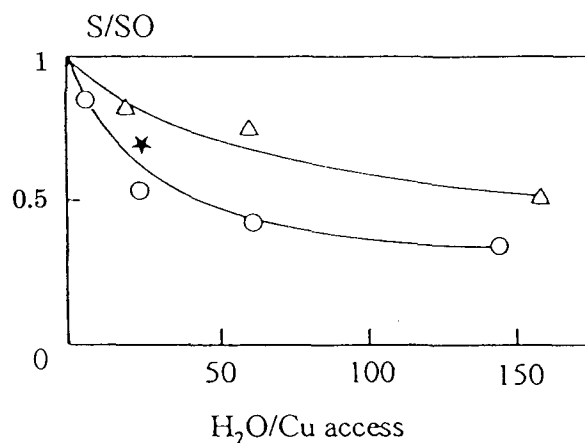
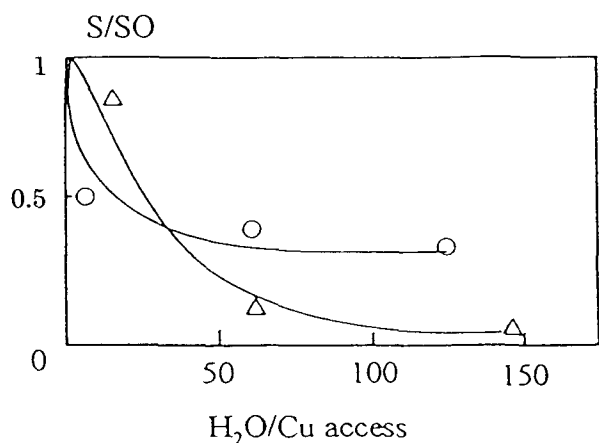


FIG. 1. CuCr(Ba)/graphite. Influence of water or ammonia on the copper surface area of CuCr(Ba)-supported catalyst. Δ , CuCr; \circ , CuCrBa. So and S designate the copper surface area before and after introduction of the modifier.

FIG. 2. CuCr(Ba)/Al₂O₃. Influence of water or ammonia on the copper surface area of CuCr(Ba)-supported catalyst. *, Experiment carried out in the presence of hydrogen; \circ , CuCr; Δ , CuCr(Ba). See Figure 1 for other details of S and So.

sufficient to maintain the catalyst in the adequate reduced state; and the inhibition of the formation of carbonaceous deposits (modification of the catalyst) or strong adsorption of some reagents and products.

In an effort to better understand the catalytic chemistry associated with this reaction, the reactivities of dodecyl nitrile and dodecylamine were measured under the same experimental conditions. The results (Table 4) show that the nitrile and the primary amine are much more easily transformed into *N*-dimethylalkylamine than either the ester or the acid (Table 5). The rate-determining step in the methylation process is directly related to one of the first reactions, which converts the ester or the acid into nitrile. It can be concluded that 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 some of the reagents.

Influence of Ca and Mn additives on the catalytic properties of CuCr/Al₂O₃(TiO₂) in the amination of dodecanoic acid. The effects of adding Ca or Mn to CuCr/Al₂O₃(TiO₂) catalysts, presented in Table 5, demonstrate that the selectivity in *N*-dimethyldodecylamine is much enhanced and that the effects are more significant

with alumina than with a titania support. Moreover, the total amine selectivity is particularly high, above 98 instead of 80%, without promoter. A similar result (Table 5) is obtained when the dodecanoic acid is replaced by methyl dodecanoate.

Reaction of laurionitrile with methanol and hydrogen in the presence of copper chromite catalysts—influence of the support. The catalytic results obtained with CuCr catalysts supported on alumina or graphite and reduced with hydrogen at 373° or 623° K are given in Table 6. In the presence of CuCr/alumina, reduced at low temperature, we noticed that didodecylamine was the major product, whereas with unreduced CuCr/graphite methylation reactions were preponderant. Selectivity [RN(CH₃)₂ + RNHCH₃ + R₂NCH₃] was 75%.

After a reduction treatment of the CuCr/Al₂O₃ catalyst at 623° K with hydrogen, the methylation reactions and the alkylation into tridodecylamine increased significantly. In the presence of the CuCr/graphite catalyst, reduced under the same conditions, mainly tridodecylamine could be observed (60%). It can be concluded that methylation of dodecylamine and didodecylamine is favored when the reduction rate of the catalyst is low, whereas it is the opposite for formation of the tridodecylamine.

SELECTIVITY CONTROL IN SUBSTITUTED FATTY AMINES SYNTHESIS

TABLE 4

Amination and *N*-Methylation of Methyl dodecanoate ($C_{11}H_{23}COOCH_3$), Hydrogenation and *N*-Methylation of Dodecyl nitrile ($C_{11}H_{23}C\equiv N$), *N*-Methylation of Dodecylamine ($C_{12}H_{25}NH_2$) in the Presence of Copper Chromite Catalysts^a

Reagent	Conversion (%)	Selectivity (%)						
		RNH ₂	RNHCH ₃	RN(CH ₃) ₂	R ₂ NH	R ₂ NCH ₃	R ₃ N	Others
Catalyst = Cu20/Cr20/TiO ₂								
Ester	97.5	31.9	30.7	20.0	2.5	2.0	2.0	10.7
$C_{11}H_{23}COOCH_3$ (a) ^b	90.0	5.2	16.5	61.0	1.5	3.5	2.0	9.9
Nitrile								
$C_{11}H_{23}C\equiv N$	100	2.0	12.9	78.0	2.7	2.9	1.5	—
Amine								
$C_{11}H_{23}CH_2NH_2$	100	—	7.3	83.3	0.8	0.9	1.9	5.8
Catalyst = Cu10/Cr10/Al ₂ O ₃								
Ester								
$C_{11}H_{23}COOCH_3$ (a) ^b	84	12.3	30.4	36.6	—	2.6	—	18.3

^aP = 50 bars, temperature = 250°C, (LHSV)_{reagent} = 1/6 h⁻¹, reagent/CH₃OH/H₂ = 1:10:50.

^bEster/NH₃/CH₃OH/H₂ = 1:10:40:100.

TABLE 5

Influence of Promoters in the Amination of Dodecanoic Acid^a

Catalyst	Acid or ester conversion (%)	Selectivity (%)				
		RNH ₂	RNHCH ₃	RN(CH ₃) ₂	RCOOMe	Others
Reaction: acid/NH ₃ /CH ₃ OH/H ₂						
CuO43/Cr ₂ O ₃ 39		100	21.2	26.0	37.1	7.0
Cu15Cr15/Al ₂ O ₃	100	20.0	32.4	26.0	8.0	13.6
Cu15Cr15Ca2/Al ₂ O ₃	100	8.4	24.0	67.0	—	0.6
Cu15Cr15Mn2/Al ₂ O ₃	100	16.0	36.0	46.0	—	2.0
Cu15Cr15Ca2/TiO ₂	100	27.0	31.0	35.6	2.1	4.3
Reaction: ester/NH ₃ /CH ₃ OH/H ₂						
Cu15Cr15Ca2/Al ₂ O ₃	100	10.0	20.8	65.7	—	3.5

^aP = 50 bar, temperature = 300°C, (LHSV)_{acid} = 1/6 h⁻¹, acid (or ester)/NH₃/CH₃OH/H₂ = 1:10:40:100.

TABLE 6

Conversion of Lauronitrile in the Presence of Copper Chromium Catalysts (effect of a support and of reduction treatment)^a

Catalyst	Conversion (%)	Selectivity (%)					
		RNHCH ₃	RN(CH ₃) ₂	R ₂ NCH ₃	R ₂ NH	R ₃ N	Others
Cu _{5.4} Cr _{5.6} /Al ₂ O ₃	95	5	15	30	22	20	8
(a),(d) ^b							
Cu _{5.4} Cr _{5.6} /Al ₂ O ₃	90	18	5	15	48	5	9
(b),(d)							
Cu _{5.9} Cr _{4.1} /graphite	95	2	3	15	15	60	5
(a),(d)							
Cu _{5.9} Cr _{4.1} /graphite	95	10	45	20	5	12	8
(c),(d)							

^aTemperature = 523°K, P = 5 MPa, RCN/CH₃OH/H₂ = 1:10:50.

^b(a), Reduction at 623°K, (b) reduction at 373°K, (c) no reduction and (d) catalytic result obtained after 25-h experiment.

On the other hand, Figures 3 and 4 show significant evolution of the conversion of dodecyl nitrile and of the selectivities of the main reaction products as a function of the reaction time. For both catalysts under consideration, a substantial decrease in selectivity in $\text{RN}(\text{CH}_3)_2$ can generally be 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 increase, which indicates that the condensation reaction of dodecylamine became faster than the hydrogenation and methylation reactions.

There can be various reasons for these changes in selectivity. However, the results in Table 6 show that changes of the temperature during the hydrogen treatment of the catalysts, supported on alumina or on graphite, lead to significant changes of selectivity, which are similar to those observed during the reaction. Moreover, pretreatment of a $\text{CuCr}/\text{Al}_2\text{O}_3$ catalyst under a hydrogen flow at 50 bar at 623°K for 12 h confirmed this hypothesis (29).

Hydrogen, therefore, plays a complex role in the transformation of nitrile, and its excess is indispensable for methylation reactions. Indeed, if a fraction of the hydrogen is replaced by nitrogen (Table 7), the reactions of substitution by methanol are almost unobserved, the main reaction being the formation of didodecylamine.

Reaction of lauronitrile with methanol and hydrogen in the presence of copper chromite/graphite catalyst—influence of barium. The catalytic properties of copper chromite catalysts can be strongly affected by the presence of additives, such as barium (29). The selectivity, however, depends a great deal on the content and on the localization of this promoter (29). Indeed, we observed that the modification of a $\text{CuCr}/\text{graphite}$ catalyst, performed by impregnation by barium, led to a different selectivity from the one obtained with a CuCrBa catalyst co-precipitated in contact with graphite (Table 8). If in both cases a substantial increase of the methylation reactions (after stabilization) can be observed, the second of the two catalysts is much more selective for dimethyldodecylamine (66%) than the former, which contains equivalent amounts of this amine and of methyl didodecylamine.

Furthermore, Figure 5 shows that the selectivity of the $\text{CuCrBa}/\text{graphite}$ catalyst still changes during the reaction, particularly at the beginning of the reaction. In the first hours of reaction, the catalyst is selective for the formation of dimethyldodecylamine ($\geq 95\%$). This selectivity drops down to 65% after 30-h reaction, and the formation of methyl didodecylamine increases. This result shows that the hydrogenating properties of the catalyst are changed during the reaction. From all our results, one may deduce that: (i) The amination and especially *N*-methylation of primary and secondary amines are favored by the presence on the surface of the catalyst of a copper chromite (CuCrO_2) phase stabilized by a well-chosen promoter. All preparation and pretreatment procedures of graphite-supported catalysts corroborate this phenomenon. (ii) Furthermore, the increase in the acidity of the support favors the production of the dialkylamine (i.e., didodecylamine) resulting from the condensation of a primary amine with the corresponding amine. (iii) The formation of tridodecylamine, which is also enhanced by the increase of acidity of the catalyst, is unexpectedly increased by the presence of metallic copper.

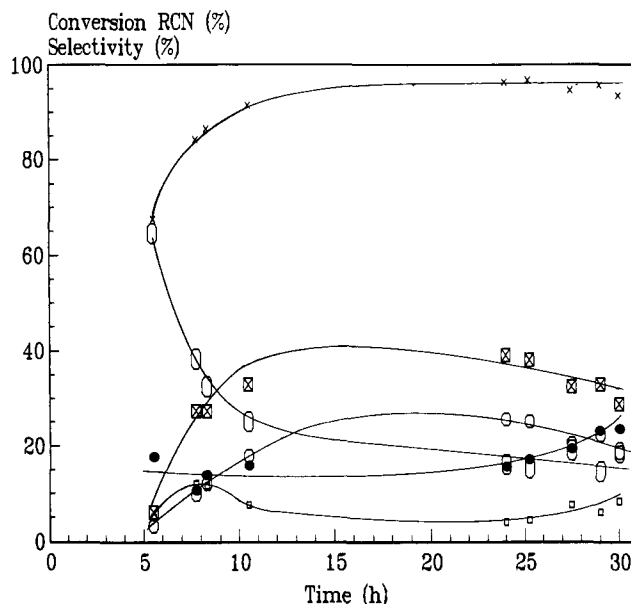


FIG. 3. Conversion of dodecyl nitrile in the presence of a $\text{CuCr}/\text{Al}_2\text{O}_3$ catalyst. Temperature = 523°K, $P = 5 \text{ MPa}$, $\text{RCN}/\text{CH}_3\text{OH}/\text{H}_2 = 1:10:50$. \circ , S.R.3N; \bullet , S.R.2NH; \boxtimes , S.R.2NMe; \circ , S.R.NMe₂; \square , S.R.NHMe; \times , conversion RCN. $\text{R}_3\text{N} = (\text{C}_{12}\text{H}_{25})_3\text{N}$; $\text{R}_2\text{NH} = (\text{C}_{12}\text{H}_{25})_2\text{NH}$; $\text{R}_2\text{NMe} = \text{C}_{12}\text{H}_{25}\text{NCH}_3$; $\text{RMe}_2 = \text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_2$; $\text{RNHMe} = (\text{C}_{12}\text{H}_{25})\text{NHCH}_3$; $\text{RCN} = \text{C}_{11}\text{H}_{23}\text{CN}$.

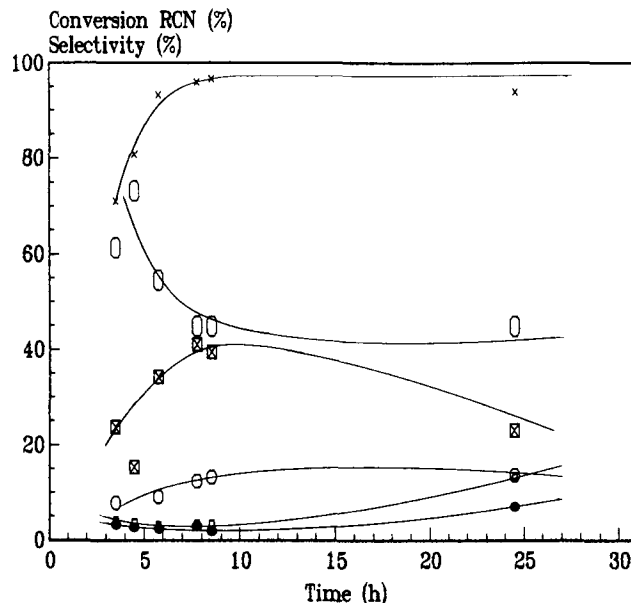


FIG. 4. Conversion of dodecyl nitrile in the presence of a $\text{CuCr}/\text{graphite}$ catalyst. Experimental conditions and key are reported in Figure 3.

Concerning *N*-methylation reactions, the promoted catalysts are initially particularly efficient for dimethyldodecylamine formation, and after stabilization there is formation of methyl didodecylamine. In reference to the usual reactional scheme (1,3), we suggest that besides the successive *N*-methylation, a new step occurs by which the carbon (methyl)-nitrogen bond is formed before the second carbon (alkyl)-nitrogen bond:

SELECTIVITY CONTROL IN SUBSTITUTED FATTY AMINES SYNTHESIS

TABLE 7

Conversion of Lauronitrile in the Presence of a CuCr/Al₂O₃ Catalyst (reduced with hydrogen at 623°K for 10 h); Influence of Hydrogen Partial Pressure^a

Reaction time (h)	Nitrile conversion (%)	Selectivity (%)					
		R ₂ NH	R ₃ N	R ₂ NCH ₃	RNHCH ₃	RN(CH ₃) ₂	Others
6	80	25	15	18	12	15	15
15	90	35	12	20	10	12	11
25	88	42	12	15	10	8	13

^aTemperature = 523°K, P = 5 MPa, RCN/CH₃OH/H₂ + N₂ = 1:10:10 + 40.

TABLE 8

Nitrile Conversion in the Presence of Barium-Promoted CuCr/Graphite Catalysts (catalysts are used without reduction treatment)^a

Catalyst	Conversion (%)	Selectivity (%)					
		RNHCH ₃	RN(CH ₃) ₂	R ₂ NCH ₃	R ₂ NH	R ₃ N	Others
Cu ₅ Cr ₄ Doped with Ba ₂	95	3	40	42	2	10	3
Cu _{5.8} Cr _{5.0} Ba _{1.2} Co-precipitated	90	—	66	—	30	3	1

^aReaction conditions as in Table 3.

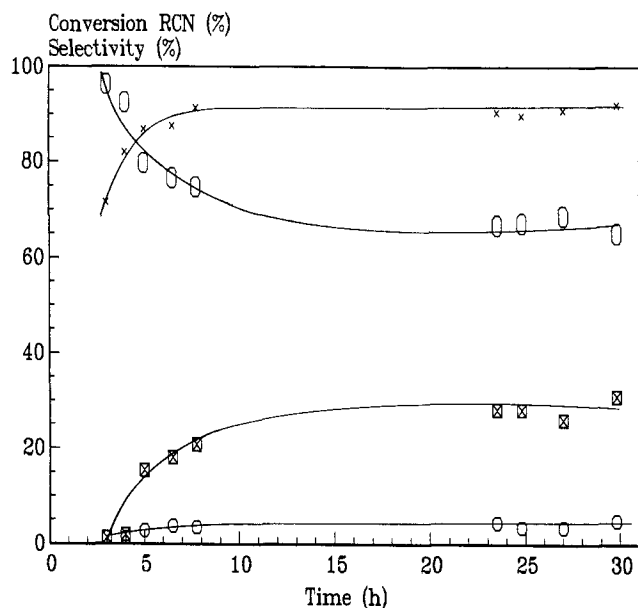
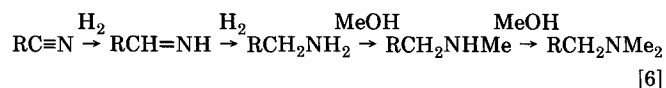
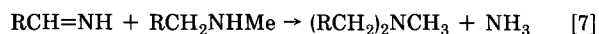


FIG. 5. Conversion of dodecyl nitrile in the presence of a CuCr-Ba/graphite catalyst. Experimental conditions and key are reported in Figure 3.



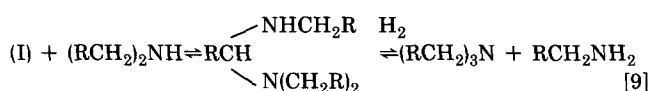
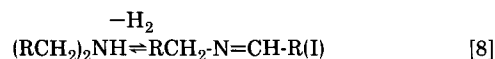
and



This scheme, rather than the methylation of didodecylamine, the rate of which is low (29), better explains the

formation of methyl didodecylamine in the presence of partially poisoned catalysts.

The increase of tertiary amine (tridodecylamine) in the presence of metallic copper is also difficult to explain from a simple alkylation reaction. We suggest that besides this reaction, tertiary amine can also result from a transalkylation reaction of the secondary amine *via* secondary imine and diamine intermediates:



During the reaction, the hydrogenating properties of the catalysts are largely modified. We have shown that these modifications could be the result of the actions of water and/or ammonia on the catalyst, which are less marked in the presence of a large excess of hydrogen (see Fig. 1).

A comparison between these variations of accessible copper surface areas and the changes in selectivity and activity as a function of running time makes a few analogies apparent. The modifications of catalytic properties are more significant at the beginning of the reaction, and also after addition of the first modifier molecules to the catalyst, variations of the surface area are the most significant. This is especially true after addition of ammonia to the nonpromoted CuCr/Al₂O₃ catalyst and of water to the CuCr/graphite catalyst. After addition of barium to the latter catalyst, addition of small amounts of water and of ammonia decreases the accessible copper surface area still more, but stabilization can then be observed, which can be connected to the change of catalytic properties.

We demonstrated that addition of a small amount of promoter (calcium, manganese, barium) increases the rates

of amination of an ester or an acid and of *N*-methylation with methanol. A specific study, starting from nitrile in the presence of alumina- or graphite-supported catalysts, also evidenced the effect of the support on activity and selectivity. A copper chromite-type catalyst significantly increases the selectivity of methylation reactions, particularly in the formation of dimethyldodecylamine.

XPS characterization of these materials seems to indicate that a copper chromite phase (CuCrO₂) is preferentially formed when graphite is used as support. Moreover, N₂O titrations show that the copper dispersion, which generally decreases in the presence of water or ammonia, is maintained after the addition of barium. These results could explain the high selectivity and stability of barium-promoted catalysts.

ACKNOWLEDGMENT

The authors of this paper thank the firm CECA (ELF-ATOCHEM) for profitable discussions and for their substantial financial aid.

REFERENCES

- Von Braun, J., G. Blessing and F. Zobel, *Chem. Ber.* 36:1988 (1923).
- Greenfield, H., *Ind. Eng. Chem. Prod. Res. Des.* 6:142 (1967).
- Volf, J., and J. Pasek, *Studies in Surface Science and Catalysis*, edited by L. Cerveny, Elsevier, p. 105, 1986.
- Pasek, J., N. Kostova and B. Dvorak, *J. Chem. Soc.* 46:1011 (1981).
- Cogez, J.L., Hydrogenation of Nitriles. Transalkylation of Amines over Metal Catalysts, University of Lille, 1981.
- Dallons, J.L., G. Jannes and A. Van Gysel, *Catalysis of Organic Reactions*, edited by W.E. Pascoe, Marcel Dekker, 1992, p. 93.
- McMillan, S., B. Pradeep and K. Agrawal, *Ind. Eng. Chem. Res.* 27:243 (1988).
- Barrault, J., M. Seffen, C. Forquy and R. Brouard, *Studies in Surface Science and Catalysis*, edited by M. Guisnet, Elsevier, 1988, p. 361.
- Barrault, J., G. Delahay, N. Essayem, Z. Gaizi, C. Forquy and R. Brouard, *Ibid.*, 1990, p. 343.
- Kliger, G.A., L.S. Glebov, R.A. Fridman, L.A. Vytново and A.N. Bashkirov, *Kinet. Katal.* 19:615 (1978).
- Baiker, A., and J. Kijenski, *Catal. Rev. Sci. Eng.* 27:653 (1985).
- Baiker, A., *Studies in Surface Science and Catalysis*, edited by M. Guisnet, Elsevier, 1988, p. 283.
- Asami, K., and K. Hashimoto, *Corrosion Sci.* 17:559 (1977).
- McIntyre, N.S., S. Sunder, D.W. Shoesmith and F.W. Stanchell, *J. Vac. Sci. Technol.* 18:714 (1981).
- Wallbank, B., C.E. Johnson and I.G. Main, *J. Elec. Spect. Relat. Phenom.* 4:263 (1974).
- McIntyre, N.S., and M.G. Cook, *Anal. Chem.* 47:2208 (1975).
- Kowalczyk, S.P., L. Ley, R.A. Pollak, F.R. McFeely and D.A. Shirley, *Phys. Rev. B* 7:4009 (1973).
- Gupta, R.P., and S.K. Sen, *Ibid.* B12:15 (1973).
- Schoen, G., and S.T. Lundin, *J. Elec. Relat. Phenom.* 1:105 (1972).
- Schoen, G., *Surf. Sci.* 35:96 (1973).
- Larson, P.E., *J. Elect. Spect.* 4:213 (1974).
- Wallbank, B., C.E. Johnson and I.G. Main, *J. Phys. C, Solid State Phys.* 6:4493 (1973).
- Kim, K.S., *J. Elec. Spect. Relat. Phenom.* 3:217 (1974).
- Brisk, M., and A.D. Baker, *Ibid.* 7:197 (1975).
- d-Huysser, A., G. Wrobel and J.P. Bonnelle, *Nouv. J. Chim.* 6:437 (1982).
- Frost, D.C., C.A. McDowell and A. Ishitani, *Mol. Phys.* 24:861 (1974).
- Duprez, D., *J. Chim. Phys.* 80:487 (1983).
- Evans, J.W., M.S.J. Wainwright, A.J. Bridgewater and D.J. Young, *Appl. Catal.* 7:75 (1983).
- Suppo-Essayem, N., Study of Supported Cu-Cr Catalysts for the Synthesis of Methylalkylamines, Thesis, University of Poitiers, ESIP, 1991.

[Received October 12, 1993; accepted June 23, 1994]