112. Activity, Selectivity, Decay and Long-Term Behaviour of Amination Catalysts

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Summary

A survey of the activity and selectivity of several catalysts for the amination of long-chain aliphatic alcohols with dimethylamine is given. The best results were obtained with Cu-catalysts whose long-term behaviour was investigated. The main reasons for catalyst decay are the irreversible adsorption of dimerization products and the thermal diffusive fusion of Cu-crystallites.

Introduction. – The activity and selectivity as well as the decay and long-term behaviour of different catalysts for the amination of long-chain aliphatic alcohols are studied, using as a test the catalytic amination of dodecanol with dimethylamine. This reaction is carried out as a one-step procedure but actually consists of several steps.

$$CH_3(CH_2)_{11}OH + NH(CH_3)_2 \xrightarrow{\text{catalyst}} CH_3(CH_2)_{11}N(CH_3)_2 + H_2O$$
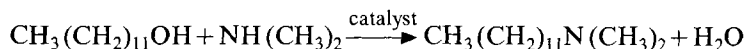
Activity and selectivity. – Most of the various types of catalysts proposed for amination are of the dehydrogenation-hydrogenation type. However, with a few exceptions these catalysts give poor selectivities or are only active enough if the reaction is carried out at high pressure. Furthermore, a quantitative comparison of the activities and selectivities of the catalysts mentioned is not reasonable because they have not been used under identical conditions. Therefore we started [1] with catalyst screening tests under identical conditions in micro-autoclaves. In order to get representative values of activities and selectivities, we varied the percentual composition and the method of preparation for each catalyst type. The results obtained are summarized in *Table 1*. Most catalyst types showed a more or less strong variation of activity and selectivity. For this reason it seemed to be more meaningful to give the ranges in which the different catalysts of the same type are active and selective.

Despite the fact that most of the catalysts tested have been proposed in the patent literature [1], only the Cu-catalysts gave good results with respect to both activity and selectivity. Ni-catalysts also showed good activity but a much lower

Table 1. *Activity and selectivity of several types of catalysts.*
(Values in parentheses indicate tendency for increasing percentage of second component. Activity and selectivity: $-\leq 0.2$, $+\geq 0.2$, $++\geq 0.4$, $+++\geq 0.6$, $++++\geq 0.8$, $+++++\geq 0.9$)

Active component	Support	Activity	Selectivity
Cr_2O_3	γ-alumina	–	+
Fe_2O_3	–	–	–
CoO	silica	+ +	+ + +
CoO	γ-alumina	+ +	+ + +
CoO/La_2O_3		+ + (+ +)	+ + + (+ +)
CoO/MoO_3	γ-alumina	+ + (+)	+ + (+)
Ni (Raney)	–	+ + +	+ +
NiO	silica	+ + +	+ + +
NiO	γ-alumina	+ + +	+ + +
NiO/CuO	silica	+ + + (+ + +)	+ + + (+ + + +)
Ru	charcoal	+	+
Rh	charcoal	+	+
Pd	charcoal	+	+
Pd	γ-alumina	+	+ +
Pt	charcoal	+	+
Pt	γ-alumina	+	+ +
CuO	γ-alumina	+ + +	+ + + + +
CuO	kaolin	+ + +	+ + + + +
CuO	silica	+ + +	+ + + + +
CuO/NiO	silica	+ + + (+ + +)	+ + + + + (+ + +)
CuO/Cr_2O_3	silica	+ + + (+ +)	+ + + + + (+ + + +)
CuO/Cr_2O_3	γ-alumina	+ + + (+ +)	+ + + + + (+ + + +)
CuO/Cr_2O_3	–	+ + + (+ +)	+ + + + + (+ + + +)
CuO/ZnO	–	+ + + (+ +)	+ + + (+ +)
ZnO	–	–	–
ZnO/Cr_2O_3	–	– (–)	– (+)
γ-alumina	–	+	+ + + +
α-alumina	–	–	+ +

Table 2. *Composition and specific surface of the Cu-catalysts used in the long-term experiments*

| Catalyst	Metal oxide content		Support	Surface
	wt % CuO	wt % Cr_2O_3		m^2/g
A	61	–	γ-alumina	59
B	47	–	koalin	43
C	25	1	silica	240

selectivity, the reason being their strong tendency for $C(1)$, $C(2)$-bond cleavage of the alcohol [2]. This $C(1)$, $C(2)$-bond cleavage was not observed to a great extent with Cu-catalysts, thus most of the intermediate aldehyde undergoes the condensation with dimethylamine instead of decarbonylation. Other long-chain aliphatic alcohols gave similar results, therefore it can be assumed that the results obtained with dodecanol are representative for most long-chain aliphatic alcohols [3].

Of all Cu-catalysts tested those given in *Table 2* proved to be the best. The corresponding results obtained in a continuous flow tubular reactor under optimum conditions are summarized in *Table 3*.

Table 3. *Experiments with catalysts A, B and C in a continuous flow tubular reactor*

	Cat. A	Cat. B	Cat. C
Amount of catalyst (g)	65	65	65
Temperature (°C)	230	230	230
Flow rates:			
Dodecanol (DOL) (g/h)	38	43	81
Dimethylamine (DMA) (g/h)	50.7	57.2	108
H_2 (sccm/s)	13.3	13.3	13.3
Molar ratio DMA/DOL	5.5	5.5	5.5
Conversion of DOL	0.98	0.96	0.96
Selectivity with respect to DIMDA	0.98	0.97	0.96
Product mixture (org. phase) wt %			
Dodecanol (DOL)	1–2	2–4	2–4
Dimethyldodecylamine (DIMDA)	97–98	94–97	93–95
Didodecylmethylamine	0.5–1	1–2	1–2
By-products	0.5–1	1–2	1–2

Catalyst decay and long-term behaviour. – The main reason for the catalyst decay during the amination was a deactivation caused by irreversibly adsorbed side-products (mainly dimerization products of the intermediate aldehyde). Details of these side-reactions have already been described [3].

$$\text{alcohol} \longrightarrow \text{aldehyde} \longrightarrow \text{product}$$
$$\downarrow$$
irreversibly adsorbed side-products.
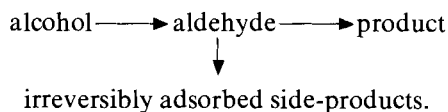
The rate of these decay reactions was strongly dependent on the surface concentration of the intermediate aldehyde which is itself related to the concentration of the alcohol in the mixture.

The decay could be observed especially during long-term experiments carried out with low molar ratios of reactants (dimethylamine/dodecanol≤ 2); at greater ratios, *i.e.* at lower alcohol concentration on the catalyst surface, the decay was not observed to an important degree. For that reason it is suggested to carry out the amination at molar ratios greater than 3.

The long-term experiments have been carried out in a continuous flow tubular reactor, with the catalysts given in *Table 2. Figure 1* shows the conversion *versus* time during the long-term tests. The corresponding selectivities remained nearly constant throughout. Catalyst types A and C showed good long-term behaviour, whereas with catalyst B a strong decrease of conversion (*i.e.* activity) was observed within the first 400 h. Since these catalysts differed above all in their support, we assumed that the decay of type B was directly related to this factor, and in order to investigate in detail the reason for this decay a number of different physical methods were applied such as N_2-adsorption, Hg-penetration, electron microscopy, electron-probe microanalysis and X-ray diffraction. The samples analysed were on one hand the unused, reduced (B_0) catalyst and on the other a deactivated sample collected after a reaction period of 400 h (B_{400}).
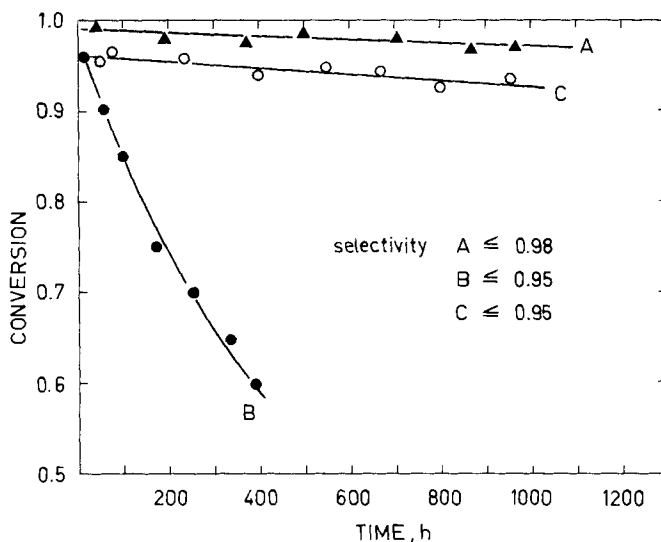
Fig. 1. *Measured conversion versus time for the catalysts A, B and C, during the long-term test.*

From N_2-adsorption measurements (BET), the observed deactivation was unlikely to have been caused by a decrease of specific surface S, since the measured values were:

$$S_{B_0} = 43 \text{ m}^2/\text{g}, \qquad S_{B_{400}} = 40 \text{ m}^2/\text{g}.$$

Figure 2 shows the integral pore-size distribution determined with a Hg-porosimeter (*Micromeritics* 915-2). There is no relation between the observed catalytic deactivation and any change of the internal macro-porous structure.

The scanning electron microscope and electron-probe microanalysis studies showed only a small difference of the macro-structure and chemical composition of the surface between B_0 and B_{400}.

From these measurements, it was concluded that the deactivation was not caused by any macro-structural changes. An important difference between the micro-structures of the active and deactivated catalyst was, however, detected by X-ray diffraction, with a diffractometer showing remarkably broader Cu-diffraction lines for the unused catalyst (B_0). From the diffraction-line broadening the mean Cu-crystallite size was calculated using the *Scherrer* equation [4]. The observed line-breadth for instrumental broadening was corrected using the curves by *Klug &* *Alexander* [4]. The crystallite size was detected from 111 reflections. *Figure 3* shows the variation of the Cu-crystallite size during the long-term experiments for catalyst types A and B *(cf. Fig. 1)*.

The size of the Cu-crystallites on catalyst B increased strongly during the long-term experiments, probably by a thermal effect, kaolin as support seeming to promote the formation of agglomerates by diffusive fusion of smaller crystallites. Cu-crystallites on both alumina and silica were much more thermally stable.
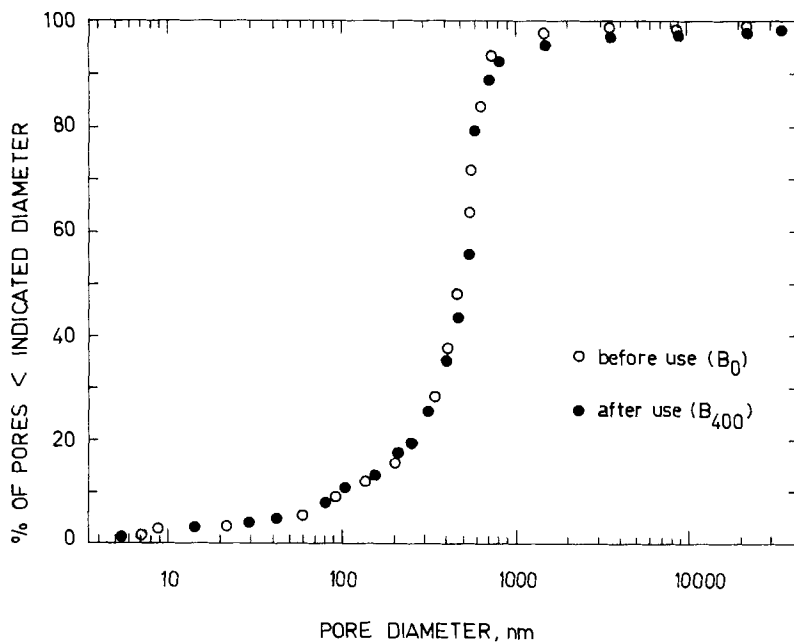
Fig. 2. *Comparison of the integral pore-size distribution for the unused* (B_0) *and the deactivated catalyst* (B_{400}).
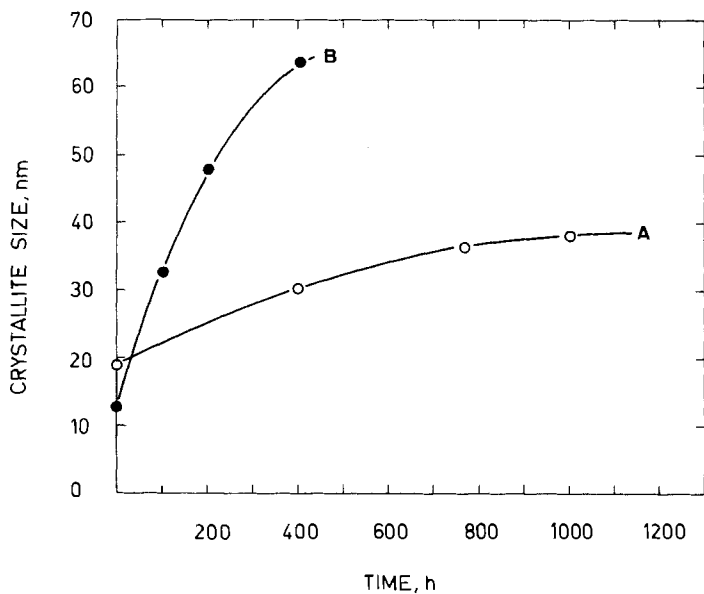
Fig. 3. *Observed variation of Cu-crystallite size during the long-term test.*

Conclusion. – Cu-catalysts proved to be very efficient for the amination of long-chain aliphatic alcohols. Catalysts which kept their activity and selectivity over 1000 h on stream have been investigated. For amination the following deactivation effects are of importance:

- irreversible adsorption of dimerization products on the active surface;
- thermal diffusive fusion of active Cu-crystallites to form larger agglomerates.

Experimental Part

The catalyst screening tests were carried out using micro-autoclaves with a capacity of 9.5 ml. The autoclaves were thermostated in a $NaNO_3$-salt bath and could be shaken mechanically. Before use, the catalysts were reduced by a mixture of H_2 and N_2 and filled into the autoclaves under argon. The screening tests were run under the following conditions: reaction temperature 300 °C; initial pressure 80 bar; molar reactant ratio DMA/DOL 1.5; reaction time 30 min.

The product mixtures were analyzed by GC. (*Perkin Elmer* 990 FID, column: 5% FFAP on chromosorb G 80/100). The continuous experiments were run using a fixed-bed reactor system. The apparatus consisted essentially of the metering systems for the reactants (dimethylamine, dodecanol and H_2), an air bath for thermostating the reactor tube (inner diameter = 2.5 cm, length = 70 cm) and of a gas chromatograph equipped with a sampling valve. In contrast to the batch experiments the continuous tests were carried out with additional H_2.

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