

# Effect of Activation Procedure and Support on the Reductive Amination of Ethanol Using Supported Cobalt Catalysts

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The reductive amination of alcohols using ammonia catalyzed by supported cobalt catalysts has been studied. The catalytic activity for ethanol conversion is shown to be directly proportional to the exposed metal surface area, indicating that the activation of ethanol is metal-catalyzed and no metal-support effects were detected. The selectivity to the mono-, di-, and triethylamine varies with temperature, reactant partial pressures, and extent of reactant conversion generally as expected for a series-type reaction scheme. Both the activation procedure and the type of support also influence selectivity. Increasing the acidity of the support favors the formation of monoethylamine, probably due to disproportionation of diethylamine on the acid sites of the support indicating the bifunctionality of the catalyst. © 1997 Academic Press

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## 1. INTRODUCTION

Ethylamines find considerable industrial application, especially as reactants in the synthesis of industrial chemical intermediates and end products (1–3). They are typically used as intermediates for the synthesis of herbicides, insecticides, pharmaceutical chemicals, textile treating chemicals, and corrosion inhibitors. Commercially, ethylamines are synthesized by contacting ethanol and ammonia over an amorphous silica–alumina catalyst at high temperatures ( $\approx 400^\circ\text{C}$ ) and high pressures ( $\approx 20$  bar) (4). The product from this process typically comprises an equilibrium controlled distribution of mono-, di-, and triethylamine, the ratio of which can be altered by adjusting the ammonia to ethanol feed ratio or by recycling unwanted products (5). Product separation frequently involves azeotropic distillation which makes this procedure costly and undesirable. This process also suffers from unwanted olefin formation caused by the acid-catalyzed dehydration of the alcohol (4).

Among several alternative methods which have been proposed for the synthesis of ethylamines, the reductive amination of ethanol is gaining increasing importance (6). The reductive amination reaction is performed at relatively low temperatures ( $\approx 200^\circ\text{C}$ ) and pressures (1–20 bar) (7) and thus offers beneficial energy implications. A large num-

ber of supported metal catalysts have been investigated for the reductive amination of alcohols but nickel, cobalt, and copper are the preferred catalysts (3, 5, 8–10). Gardner and Clark (3) claimed a higher activity of supported cobalt catalysts in comparison to supported nickel catalysts in the reductive ethanol amination using catalysts with high metal loadings. In a previous work (10) we showed that the intrinsic activity of a Co/SiO<sub>2</sub> catalyst was higher than of Ni/SiO<sub>2</sub>. The higher activity of the supported cobalt catalyst was combined with a higher selectivity toward the industrial desired mono- and diethyl amine.

As in the case of the acid-catalyzed amination of alcohols, the separation and recycling of unwanted amines is necessary to meet industrial requirements. The product selectivities are controlled kinetically and may be adjusted by altering the reactant ratio or the hydrogen partial pressure (10).

In order to increase the efficiency of metal catalysts, they are frequently supported on high-surface-area carriers. It has become clear, however, that both the activity and the selectivity of many heterogeneous catalytic reactions also depend on the nature of the support (11–13). The reason for this is not always obvious and the influence of a number of factors needs to be investigated in order to describe the observed phenomena. These support effects may be due to changes in metal particle sizes and morphologies, or due to electronic interactions between the carrier and the supported metal crystallites. In addition to these effects, incomplete reduction of the metal, bifunctional catalysis, and spillover phenomena must be considered.

Jiratova *et al.* (14) showed that the reductive amination of diethylene glycol over supported nickel catalysts, yielding morpholine with diethylene glycolamine as an intermediate, is catalyzed by both the metal and the support, indicating bifunctional catalysis. The initial activation of diethylene glycol was proportional to the number of exposed metal atoms but the subsequent conversion of diethylene glycol amine seemed to be a function of the acidity of the support.

Since supported cobalt is the preferred catalyst for the reductive amination of ethanol (3, 10) and cobalt-support

interactions are known to influence both activity and selectivity during CO hydrogenation (15), this work was initiated in order to investigate whether the type of metal carrier influenced the catalytic performance of supported cobalt for the reductive amination of ethanol. Besides varying the type of support, the time and temperature of reduction were varied in order to determine the significance of the extent of reduction and the metal particle size on the ethanol amination with ammonia.

## 2. EXPERIMENTAL

All catalysts used in this study were prepared by incipient wetness impregnation using an aqueous solution of cobalt nitrate. The concentration of the impregnation solutions were adjusted to obtain a cobalt loading of 9 wt%. This loading is a compromise between dispersion and reducibility for the silica-supported catalysts (16). The silica and magnesia supports were supplied by Merck (Darmstadt, Germany) and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were supplied by Kali-Chemie (Hannover, Germany). The physical characteristics of the supports are given in Table 1. The cobalt nitrate precursor (Co(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O) was supplied by Merck and had a purity greater than 98%. Following impregnation, the catalysts were dried under air at 100°C for 16 h before storage in a desiccator.

The catalysts were reduced in hydrogen prior to the use of the catalysts in the reductive amination of ethanol with ammonia. The extent of reduction of cobalt in the catalyst samples was determined using a combined TPR/TPO technique (17). With this technique the amount of zerovalent cobalt, oxidizable divalent, and nonoxidizable divalent cobalt can be determined. The procedure involved initial reduction of ca. 0.5 g of the catalyst precursor in a 60 ml (NTP)/min stream of H<sub>2</sub> using a temperature programming rate of 10°C/min in a TPR cell. The time and temperature of reduction could be adjusted as required. Subsequently, oxidation of the reduced catalyst was performed in a 60-ml (NTP)/min stream of 2% O<sub>2</sub>/He as the temperature was raised linearly

from 50 to 1000°C at 10°C/min. Oxygen concentrations in the effluent were measured with a thermal conductivity detector using a 60-ml (NTP)/min stream of He as a reference. The TCD was calibrated by temperature-programmed oxidation of pure metallic Co.

Metal surface areas were determined using a Micromeritics ASAP 2000 chemisorption apparatus. The procedure involved *in situ* reduction of ca. 0.5 g of the catalyst precursor in a 60-ml (NTP)/min stream of H<sub>2</sub> under conditions identical to those used prior to the amination reaction. Following reduction, the catalyst was evacuated at 400°C until the pressure was less than 0.15 Pa. The catalysts were then cooled under vacuum to the adsorption temperature and the hydrogen uptake was measured. The adsorption isotherms were measured at 100°C for the SiO<sub>2</sub>- and MgO-supported catalysts and at 125°C for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-supported catalysts. Elevated temperatures for the hydrogen chemisorption were used because of the activated nature of hydrogen chemisorption on cobalt (18). The metal dispersion was defined as the number of metal atoms exposed to the gas phase relative to the total number of metallic cobalt atoms present in the reduced catalyst as determined by the combined TPR/TPO technique. For the calculation of the average particle diameter it was assumed that reduced cobalt and nonreduced cobalt form different phases (19). Using a density of 8.9 g/cm<sup>3</sup> (20) and assuming spherical metallic cobalt particles the average diameter of the metallic particles can be calculated.

The gas-phase amination of ethanol was studied in an atmospheric-pressure, continuous-flow stainless steel reactor with on-line gas chromatographic separation and a TCD. The experimental apparatus has been described in detail elsewhere (10). Prior to the experiments the catalyst was reduced *in situ* in a 60-ml (NTP)/min H<sub>2</sub> stream using a temperature programming rate of 10°C/min to reach the reduction temperature. The time and temperature of reduction were varied as required. Following reduction, the catalyst was cooled down to 100°C in hydrogen at which time the feed stream was diverted through the reactor bypass and the feed system was stabilized. When comparing catalysts the molar feed ratio of ethanol : ammonia : hydrogen : nitrogen was maintained at 1 : 2 : 8.6 : 17.1. Mass balances were calculated using nitrogen as an internal standard and the agreement of mass flows was within 5%. Upon stabilization of the feed delivery system (as confirmed by gas chromatographic analysis), the feed was diverted downward through the reactor and the reactor temperature was raised linearly at 10°C/min from 100 to 180°C. The catalyst was allowed to stabilize at 180°C and 1 bar for 24 h before collection of data was started. The catalytic activity and selectivity were quite stable following this start-up period. Space velocities were changed allowing for catalyst comparison at similar conversions (WHSV = 0.5–2.0 g<sub>EtOH</sub>/g<sub>cat</sub> · h).

TABLE 1

Physical Characteristics of the Carrier Materials

Support	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	Al <sub>2</sub> O <sub>3</sub> content (wt%)
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	209	0.45	85	100
SiO <sub>2</sub>	289	1.16	160	0
MgO	33	0.14	148	0
SiO <sub>2</sub> -1 Al <sub>2</sub> O <sub>3</sub>	491	1.21	98	1
SiO <sub>2</sub> -4 Al <sub>2</sub> O <sub>3</sub>	563	0.82	58	4
SiO <sub>2</sub> -9 Al <sub>2</sub> O <sub>3</sub>	461	0.48	42	9
SiO <sub>2</sub> -13 Al <sub>2</sub> O <sub>3</sub>	516	0.47	36	13

## 3. RESULTS

*Physical Characterization of Freshly Reduced Catalysts*

The influence of the reduction time and temperature and carrier on the physical characteristics of the cobalt in the reduced catalysts is given in Table 2. Increasing the time of reduction at 500°C for Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> increases the extent of reduction, metal surface area, and crystallite size, indicating some sintering at 500°C. The observed increase in the extent of metal reduction is due to the increased reduction of oxidizable cobalt. Increasing the reduction temperature at a reduction time of 1 h for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts increases the extent of reduction and the metal crystallite size, although the amount of nonoxidizable Co and metal surface area show a maximum due to sintering. The physical characteristics of cobalt in the freshly reduced Co/SiO<sub>2</sub> and Co/SiO<sub>2</sub>-1 Al<sub>2</sub>O<sub>3</sub> are similar as expected on the basis of the low alumina content (1 wt%) in the silica-alumina carrier. Increasing the alumina content in the silica-alumina carrier caused a decrease in the extent of reduction with a significant increase in the amount of nonoxidizable Co. This has been ascribed to the formation of cobalt-support species (17). Increasing the alumina content in these carriers also increases the metal particle size. It might be speculated that during impregnation some cobalt will be associated with the acid sites of these supports and this cobalt will act as an anchor for other reducible cobalt species. The extent of reduction for Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under the same reduction conditions is lower than that for Co/SiO<sub>2</sub> due to the larger amount of oxidizable Co species formed in the preparation step in the case of an alumina support. The reduced Co/MgO catalysts did not show any reduced cobalt metal.

*Catalyst Deactivation Behavior*

Figure 1 illustrates the time on stream behavior of the ethanol amination using ammonia over Co/Al<sub>2</sub>O<sub>3</sub>. For this experiment relative to the experiments for catalyst comparison the hydrogen partial pressure was reduced, and the ethanol and ammonia partial pressures were increased to show the effect of deactivation more clearly. A considerable change in both activity and selectivity occurs in the first 24 h. With decreasing activity, a decrease in the degree of amine substitution is observed, so that the selectivity to diethylamine and triethylamine decreases and the selectivity to monoethylamine increases, which is expected for a series-type reaction. Catalyst deactivation during amination has been shown to be caused by metal nitride formation, metal carbide formation, deposition of carbonaceous material, and the thermal diffusive fusion of the supported metal crystallites (6, 21-24). Hydrogen prevents the metal nitride formation. A study on the effect of the hydrogen partial pressure showed a rapid change in activity and selectivity with no long-term effects (10, 25) and the deactivation during the initial 24 h therefore cannot be attributed to nitride formation. Since deactivation by metal crystallite agglomeration was found to be significant only if low-surface-area supports were used (21), the observed decrease in ethanol conversion is probably caused by metal carbide formation and deposition of carbonaceous material.

The changes in the ethylamine selectivity with time on stream could possibly be due to changes in catalyst morphology, possibly caused by incorporation of carbon into the metal crystallites. It is more likely, however, that these changes are due to the decreasing ethanol conversion. Monoethylamine selectivity decreases and diethylamine and

TABLE 2

**Influence of Carrier, Reduction Temperature, and Time on the Physical Characteristics of Cobalt in the Reduced Cobalt Catalysts (9 wt% Co on Support)**

Catalyst	$T_{\text{red}}$ (°C)	$t_{\text{red}}$ (h)	Reduced Co (mol/mol Co)	Oxidizable Co (mol/mol Co)	Nonoxidizable Co (mol/mol Co)	Metal surface area (m <sup>2</sup> /g)	Metal dispersion (%)	Crystal size (nm)
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	500	1	0.08	0.65	0.27	0.59	14.7	6.7
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	500	5	0.29	0.58	0.13	0.69	4.7	20.5
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	500	20	0.40	0.38	0.22	0.79	4.0	24.1
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	300	1	0.01	0.72	0.27	0.13	25.9	3.7
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	400	1	0.04	0.70	0.26	0.33	14.9	7.3
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	450	1	0.06	0.79	0.15	0.51	16.3	5.9
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	550	1	0.15	0.53	0.32	0.42	5.7	16.8
Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	600	1	0.27	0.25	0.48	0.38	2.9	33.7
Co/SiO <sub>2</sub>	500	1	0.42	0.29	0.29	1.68	8.1	12.2
Co/MgO	500	1	≈ 0	0.84	0.16	≈ 0	—	—
Co/SiO <sub>2</sub> -1 Al <sub>2</sub> O <sub>3</sub>	500	1	0.46	0.44	0.10	1.83	8.6	12.1
Co/SiO <sub>2</sub> -4 Al <sub>2</sub> O <sub>3</sub>	500	1	0.40	0.40	0.20	1.15	5.8	16.6
Co/SiO <sub>2</sub> -9 Al <sub>2</sub> O <sub>3</sub>	500	1	0.35	0.34	0.31	0.74	4.3	22.6
Co/SiO <sub>2</sub> -13 Al <sub>2</sub> O <sub>3</sub>	500	1	0.32	0.24	0.44	0.24	1.5	64.8

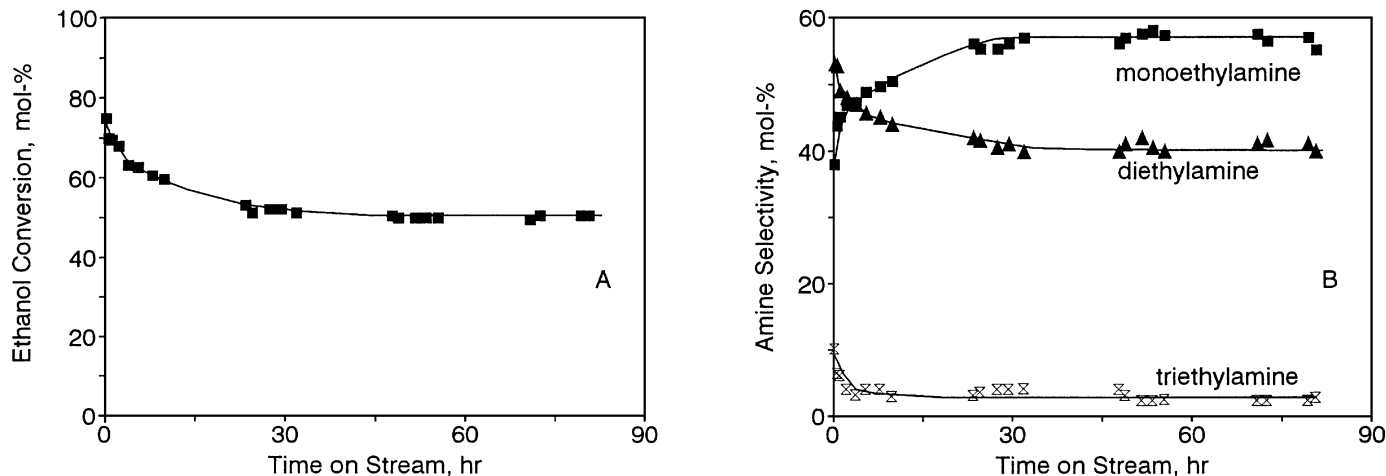


FIG. 1. Time on stream behavior of the reductive amination of ethanol over  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  reduced at  $500^\circ\text{C}$  for 1 h (reaction conditions:  $T=180^\circ\text{C}$ ,  $p=1$  bar,  $\text{WHSV}=1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{catalyst}} \cdot \text{h}$ ; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2=1:2:4:13.6$ ). (A) Ethanol conversion. (B) Selectivities of the individual ethylamines.

triethylamine selectivities increase with increasing reaction temperature, ethanol conversion, ethanol to ammonia feed ratio, and hydrogen partial pressure (5, 7, 10). The decreasing ethanol conversion with time on stream would thus be expected to result in higher monoethylamine and lower diethylamine and triethylamine selectivities, which is observed experimentally.

#### Effect of Reduction Time

Figure 2A shows the influence of reduction time on the activity of the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  for the reductive amination of ethanol as measured by the conversion of ethanol at  $\text{WHSV}=1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{cat}} \cdot \text{h}$ . Increasing the time of reduction at  $500^\circ\text{C}$  from 1 to 5 h results in a significant increase in the activity of the catalyst. This increase is accompanied by

an increase in the metal surface area of the freshly reduced catalyst (see Table 1). Increasing the reduction time from 5 to 20 h does not result in any increase in ethanol conversion, even though the metal surface area increases. However, during the stabilization period this catalyst showed a slightly stronger deactivation.

Figure 2B shows the effect of the reduction time on the selectivity of the ethylamines at an interpolated ethanol conversion of 50%. The selectivity to monoethylamine decreases slightly and the selectivity to both diethylamine and triethylamine increases slightly with time of reduction. Because all selectivities are compared at the same conversion, the extent of reaction therefore cannot be the cause of the observed changes in selectivity. Changes in the properties of the catalyst must thus cause the differences in the selectivity.

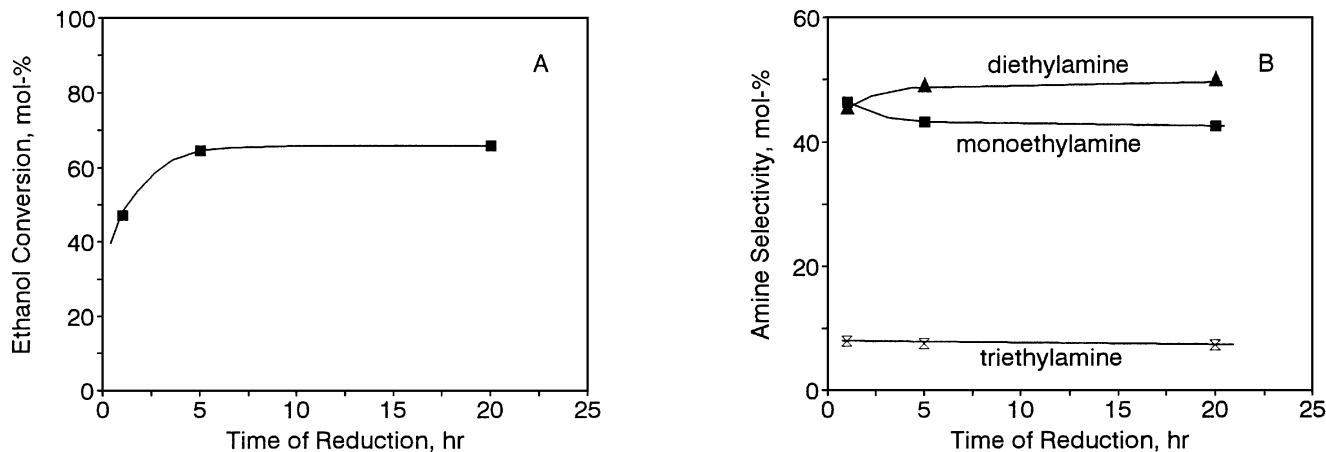


FIG. 2. Effect of reduction time on the reductive amination of ethanol over  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  reduced at  $500^\circ\text{C}$  (reaction conditions:  $T=180^\circ\text{C}$ ,  $p=1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2=1:2:8.6:17.1$ ). (A) Ethanol conversion at  $\text{WHSV}=1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{catalyst}} \cdot \text{h}$ . (B) Selectivities of the individual ethylamines interpolated to an ethanol conversion of 50%.

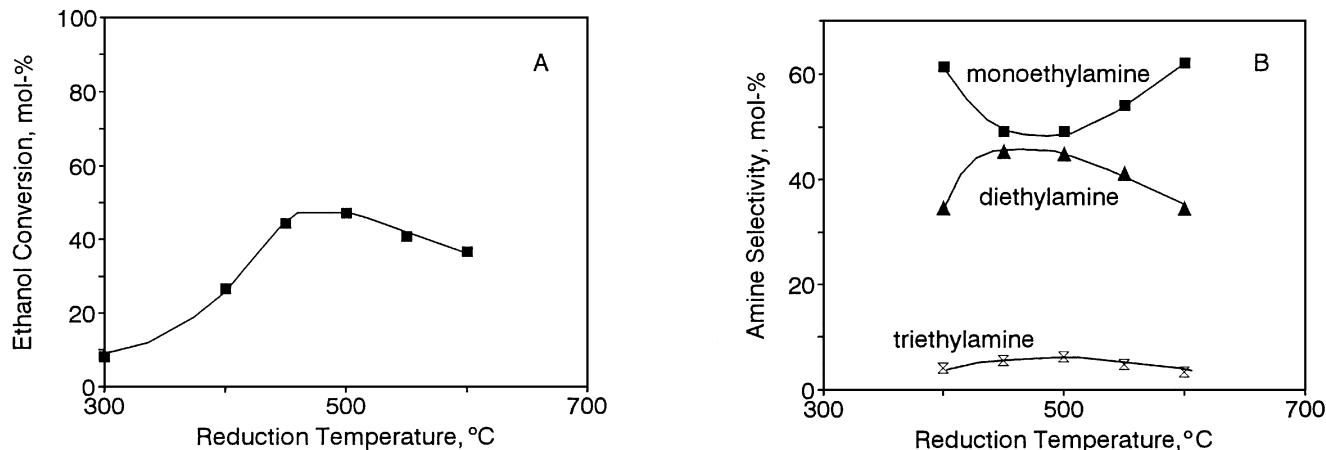


FIG. 3. Effect of reduction temperature on the reductive amination of ethanol over  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  reduced for 1 h (reaction conditions:  $T = 180^\circ\text{C}$ ,  $p = 1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2 = 1:2:8.6:17.1$ ). (A) Ethanol conversion at  $\text{WHSV} = 1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{catalyst}} \cdot \text{h}$ . (B) Selectivities of the individual ethylamines interpolated to an ethanol conversion of 35%.

### Effect of Reduction Temperature

The influence of reduction temperature on the conversion of ethanol in the reductive amination on  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  at  $\text{WHSV} = 1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{cat}} \cdot \text{h}$  is shown in Fig 3A. The ethanol conversion as a function of the reduction temperature passes a maximum at a reduction temperature in the range of 450–500°C. A similar trend is observed for the metal surface area as measured using hydrogen chemisorption as a function of the reduction temperature. This is caused by the increased degree of reduction and the increased extent of sintering.

The selectivity to individual ethylamine product compounds interpolated to 35% ethanol conversion varies significantly with reduction temperature (see Fig. 3B; the selectivity with the catalyst reduced at 300°C could not be determined accurately at this level of conversion due to its low activity). Monomethylamine selectivity first decreases and then increases, while diethylamine and triethylamine selectivities show the opposite trend. Since the selectivities are being compared at the same interpolated level of ethanol conversion and under the same reaction conditions, the change in the selectivities must be attributed to changes in the state of the supported cobalt catalysts.

### Effect of Metal Support

A comparison of the performance of a number of supported cobalt catalysts was conducted in order to determine the influence of the carrier on the activity and selectivity during the amination reaction (see Table 3). Neutral ( $\text{SiO}_2$ ), acidic ( $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ), and basic ( $\text{MgO}$ ) supports were used to determine whether the support has any bifunctional activity or whether cobalt-support interactions influence the amination reaction.

The ethanol conversion decreased from 66 to 47 to 2% as the cobalt support is changed from  $\text{SiO}_2$  to  $\gamma\text{-Al}_2\text{O}_3$  to

$\text{MgO}$ . The decrease in activity corresponds to the decrease in the measured metal surface area as measured by hydrogen chemisorption. The low metal surface area of the  $\text{MgO}$ -supported catalyst is due to the low extent of metal reduction and indicates that the divalent cobalt is not active for the reductive amination reaction. Increasing the aluminium content in a range of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  supports results in a decrease in the ethanol conversion. The decrease in activity is concurrent with a decrease in the metal surface area. For silica-alumina supports with a low aluminium content, the ethanol conversion approaches that of the pure  $\text{SiO}_2$ -supported catalyst.

Changing the type of carrier results in changes in the product selectivity during the reductive amination of

TABLE 3

Effect of Support on Activity and Selectivity of the Reductive Amination of Ethanol Using Ammonia<sup>a</sup>

Catalyst	$X_{\text{EtOH}}^b$ (mol%)	$S_{\text{MEA}}^{c,d}$ (mol%)	$S_{\text{DEA}}^{c,e}$ (mol%)	$S_{\text{TEA}}^{c,f}$ (mol%)
$\text{Co}/\text{SiO}_2$	66.2	49.5	41.1	9.4
$\text{Co}/\gamma\text{-Al}_2\text{O}_3$	47.2	46.5	45.6	7.9
$\text{Co}/\text{MgO}$	1.7	— <sup>g</sup>	— <sup>g</sup>	— <sup>g</sup>
$\text{Co}/\text{SiO}_2\text{-1 Al}_2\text{O}_3$	65.5	50.5	41.6	7.9
$\text{Co}/\text{SiO}_2\text{-4 Al}_2\text{O}_3$	52.4	51.1	39.5	9.4
$\text{Co}/\text{SiO}_2\text{-9 Al}_2\text{O}_3$	41.6	52.6	37.5	9.9
$\text{Co}/\text{SiO}_2\text{-13 Al}_2\text{O}_3$	36.6	64.3	30.6	5.1

<sup>a</sup> 9 wt% Co on support reduced in 60 ml(NTP)/min  $\text{H}_2$  at 500°C for 1 h;  $T_{\text{reaction}} = 180^\circ\text{C}$ ;  $p = 1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2 = 1:2:8.6:17.1$ .

<sup>b</sup> Ethanol conversion at  $\text{WHSV} = 1 \text{ g}_{\text{EtOH}}/\text{g}_{\text{cat}} \cdot \text{h}$ .

<sup>c</sup> Selectivities interpolated at an ethanol conversion of 50%.

<sup>d</sup> MEA, monoethylamine.

<sup>e</sup> DEA, diethylamine.

<sup>f</sup> TEA, triethylamine.

<sup>g</sup> Activity too low to determine selectivity at 50% ethanol conversion.

ethanol. Most notably, it is observed that increasing the aluminium content in the  $\text{SiO}_2\text{-Al}_2\text{O}_3$ -supported cobalt catalysts results in an increase in the monoethylamine selectivity and a decrease in the selectivity to diethylamine and triethylamine. The silica-alumina support with only 1 wt%  $\text{Al}_2\text{O}_3$  shows product selectivities similar to those obtained with the  $\text{SiO}_2$ -supported cobalt catalyst (*vide supra*). The composition of the support therefore appears to influence the product selectivity.

#### 4. DISCUSSION

Measurement of the metal surface area and the distribution of different cobalt species in the reduced catalyst were conducted with a freshly reduced catalyst, whereas evaluation of catalytic performance was measured after at least 24 h on stream. Differences in the extent of deactivation in this initial period might cause errors when comparing catalytic activity. However, the deactivation profiles of the catalysts tested were similar.

The formation of metallic cobalt was inhibited severely when using magnesia as a support. With this catalyst, hardly any activity in the reductive amination of ethanol was observed, indicating the necessity of zerovalent cobalt species in the catalyst. Both the extent of reduction and the metal dispersion are known to be affected considerably by the method of catalyst pretreatment and by the type of carrier used. The use of silica as a carrier was found to result in the most efficient amination catalyst, principally due to increased extent of metal reduction. With the  $\gamma\text{-Al}_2\text{O}_3$  support, and more particularly the  $\text{MgO}$  support, the reduction of supported cobalt was inhibited and this resulted in less active catalysts because of the lower reduced metal surface

area. Increasing the time of reduction results in increased metal surface areas due to increased extent of hydrogen reduction. The catalytic activity is affected considerably by the temperature of hydrogen reduction and an optimum in catalytic activity was recorded at a reduction temperature of ca.  $500^\circ\text{C}$ . At lower temperatures the extent of metal reduction was low, and at higher temperatures, metal particle agglomeration resulted in lower reduced metal surface areas.

Plotting the measured surface area versus the activity for ethanol conversion (taken as the interpolated, average rate at an overall ethanol conversion of 50%) shows roughly a linear correlation, independent of the type of carrier (Fig. 4A). The linear nature of this plot indicates that reduced cobalt metal is most likely to be the active catalytic component. This is substantiated by the very low activity of  $\text{Co/MgO}$  which consists mainly of divalent oxidizable  $\text{Co}$ . It also indicates that the support does not contribute significantly toward the conversion of the reactant ethanol. The support helps to disperse and stabilize the active metallic phase, but down to a metal particle size of 5.9 nm no metal-support interaction could be observed. The scatter in the data is most likely caused by difficulties in recording the metal surface areas of the supported cobalt catalysts (18), the interpolation procedure used for obtaining the average rate and small differences in the initial deactivation behavior. Highly active, dispersed cobalt catalysts for the reductive amination of ethanol may therefore be obtained by producing small metal particles on the support directly either by decomposition of a zero valent metal complex (26) or by electroless plating (27).

It was expected that if the reaction is solely catalyzed by the metal and that all reactions are structure insensitive,

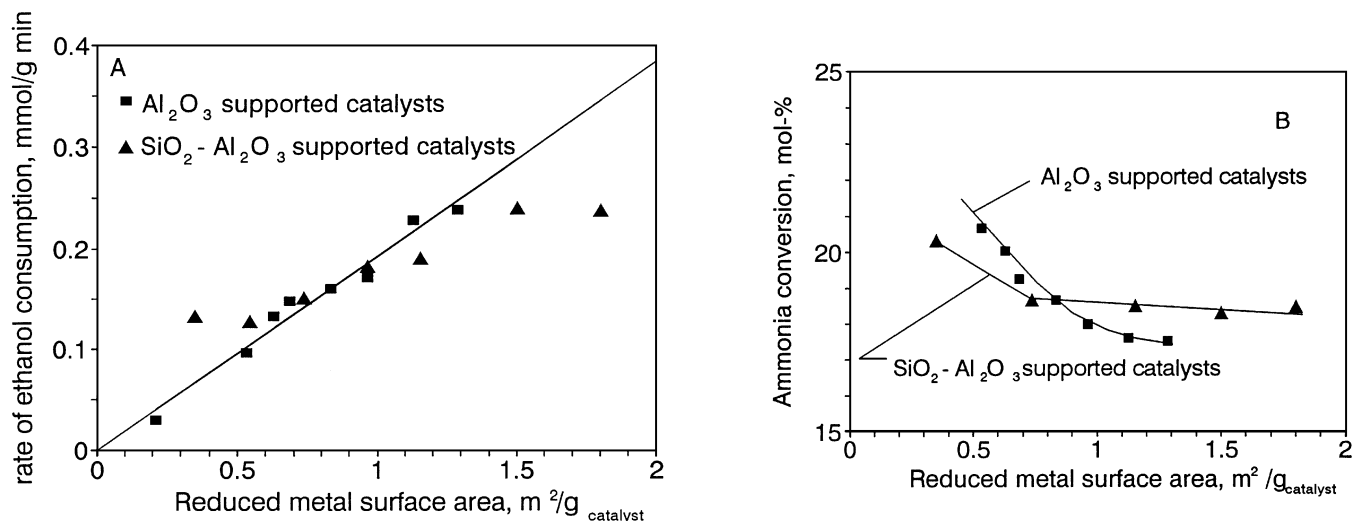


FIG. 4. Effect of the reduced metal surface area on the activity of supported cobalt catalysts in the reductive amination of ethanol (reaction conditions:  $T = 180^\circ\text{C}$ ,  $p = 1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2 = 1:2:8.6:17.1$ ). (A) Average rate of ethanol consumption at an interpolated ethanol conversion of 50%. (B) Ammonia conversion at 50% an interpolated ethanol conversion of 50%.

the ammonia conversion at an ethanol conversion of 50% would be constant. Figure 4B shows the change in ammonia conversion as a function of reduced metal surface area. The catalyst with an alumina support shows behavior different from that of the catalysts with a silica–alumina support. For both type of carriers an increase in the ammonia conversion is observed with decreasing metal surface area. Since the ethanol conversion is constant, the stoichiometric factor of the reaction has been changed by varying the reduced metal surface area. The metal surface area decreases with increasing aluminium content in the silica–alumina catalyst. Increasing the aluminium content in amorphous silica–alumina generates a larger number of acid sites in the support. It might therefore be speculated that the increase in the number of acid sites might be associated with the increase in ammonia conversion.

The change in ammonia conversion at a constant level of ethanol conversion is accompanied by a change in ethylamine selectivity. The metal dispersion or the average diameter of supported metal crystallites has been found previously to be an important parameter in the instance of structure-sensitive reactions. For example, both the specific activity and the selectivity during CO hydrogenation using supported cobalt catalysts was found to be dependent on the metal dispersion (28). Increasing the temperature or time of hydrogen reduction results in a decrease in the dispersion of metallic cobalt. Monoethylamine selectivity first decreases and then increases with increasing temperature of hydrogen reduction and decreases with increasing time of reduction at 500°C. Thus there is no correlation between measured ethylamine selectivity and the dispersion of the metallic cobalt crystallites.

The presence of unreduced cobalt oxide intimately intermixed with reduced cobalt metal is expected to change

the electronic nature of supported catalysts due to the electronegative nature of oxygen. A change in the electronic nature of supported cobalt will be expected to alter the strength of adsorption of both reactants and reaction intermediates and therefore affect product selectivity. However, it would also affect the rate of ethanol consumption which was shown to be linearly dependent on the reduced metal surface area, independent of the type of carrier (see Fig. 4A). Moreover, no correlation could be found between the observed monoethylamine selectivity and the amount of nonreduced cobalt. The presence of unreduced cobalt intermixed with metallic cobalt therefore cannot explain the observed change in product selectivity. This finding is in agreement with the finding of Chin and Hercules (19) that, on reduced  $\text{Co}/\text{Al}_2\text{O}_3$ , cobalt metal and unreduced cobalt (in the form of surface aluminate) are probably two separate phases.

The relative rates of amine formation, i.e., rate of diethylamine formation to rate of monoethylamine formation ( $r_{\text{DEA}}/r_{\text{MEA}}$ ) and rate of triethylamine formation to rate of diethylamine formation ( $r_{\text{TEA}}/r_{\text{DEA}}$ ), follow distinct trends when plotted against reduced metal surface area of the supported cobalt catalysts (see Fig. 5). With the alumina-supported catalyst a linear dependency of the rate of formation of diethylamine relative to the rate of formation of monoethylamine was observed. The relative rate of formation of triethylamine to diethylamine was within the error of measurement independent of the reduced metal surface area. This might indicate that more surface species are involved in the rate-determining step for the formation of diethylamine and triethylamine than for the formation of monoethylamine. The observed linear relationship between the rate of ethanol conversion and reduced metal surface area is in contradiction with this conclusion.

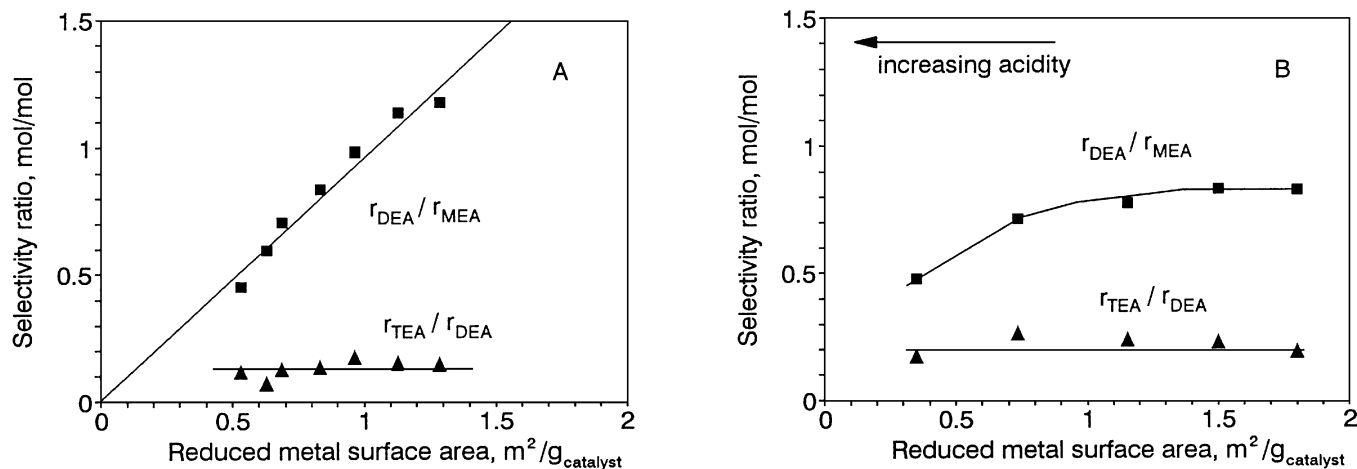
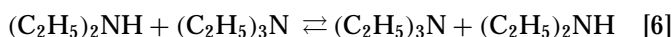
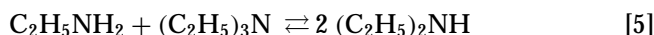
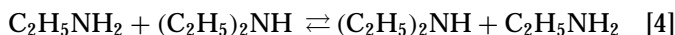
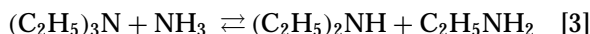
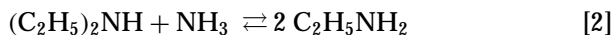
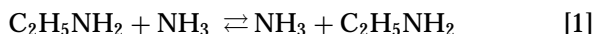


FIG. 5. Effect of the reduced metal surface area on the selectivity ratio of the rate of formation of diethylamine ( $r_{\text{DEA}}$ ) to monoethylamine ( $r_{\text{MEA}}$ ) and of triethylamine ( $r_{\text{TEA}}$ ) to diethylamine ( $r_{\text{DEA}}$ ) in the reductive amination of ethanol at an interpolated ethanol conversion of 50% over supported cobalt catalysts (reaction conditions:  $T=180^\circ\text{C}$ ,  $p=1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2=1:2:8.6:17.1$ ). (A) Alumina-supported cobalt catalyst. (B) Silica–alumina-supported cobalt catalysts.

Moreover, this explanation should be independent of the type of carrier, but with the silica-alumina no linear correlation between the relative rate of diethylamine formation to monoethylamine formation and the reduced metal surface area was observed (Fig. 5B). With this type of support the relative rates of triethylamine to diethylamine formation were also found to be independent of the reduced metal surface area within the experimental error.

With increasing aluminium content in the silica-alumina support the acidity of the support increases and the extent of reduction decreases. The product amines are bases like the reactant ammonia ( $pK_b$ , monoethylamine = 3.29,  $pK_b$ , diethylamine = 3.00,  $pK_b$ , triethylamine = 3.25 (29), and  $pK_b$ , ammonia = 4.75) and can therefore adsorb on an acidic support. The acid-catalyzed amination of ethanol over  $\text{SiO}_2\text{-}13\text{Al}_2\text{O}_3$  requires a reaction temperature of at least  $375^\circ\text{C}$  (16), indicating that the reaction between adsorbed ammonia and ethanol does not occur at reaction temperatures of  $180^\circ\text{C}$ . Therefore the reaction of the product amines with gas-phase ethanol is not likely to occur. The following disproportionation reactions with one of the two reactants adsorbed on the acid support might occur.



One of the two reactants and one of the two product compounds is an adsorbed species on the acidic support.

Reactions [1], [4], and [6] are identities in which only the type of adsorbed species changes, but they do not influence the product selectivity. The reactions with ammonia are most likely since it is the most abundant gas-phase compound and the least sterically hindered compound. These reactions yield monoethylamine and might explain the observed increase in the rate of formation of monoethylamine relative to the formation of diethylamine and triethylamine with increasing number of acid sites on the support. If acid-catalyzed disproportionation reactions cause the increase in the monoethylamine yield with increasing acidity, a more complex relationship between the relative rate of formation of triethylamine to diethylamine and the acidity of the support is expected. The observed ratio of triethylamine formation to diethylamine formation does not contradict this, but more accurate data are necessary to establish that relationship.

In the instance of  $\text{Al}_2\text{O}_3$ -supported cobalt catalysts in which the time and temperature of hydrogen reduction were varied, the rate of diethylamine formation relative

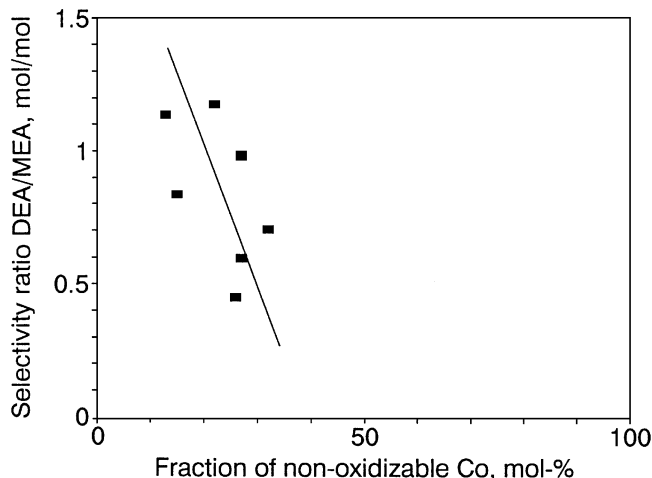


FIG. 6. Effect of the amount of nonoxidizable cobalt species on the selectivity ratio of the rate of formation of diethylamine ( $r_{\text{DEA}}$ ) to monoethylamine ( $r_{\text{MEA}}$ ) at an interpolated level of ethanol conversion of 50% over  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  (reaction conditions:  $T=180^\circ\text{C}$ ,  $p=1$  bar; feed composition,  $\text{EtOH}:\text{NH}_3:\text{H}_2:\text{N}_2=1:2:8.6:17.1$ ).

to monoethylamine formation varies linearly with the reduced metal surface area. Increasing the extent of reduction reduces the amount of divalent cobalt species which may act as acid sites. No correlation could be observed between the ethylamine selectivity and the amount of oxidizable divalent cobalt species. Figure 6 shows indications of a weak correlation between the relative rate of formation of diethylamine to monoethylamine at 50% ethanol conversion and the relative amount of nonoxidizable cobalt in the catalyst. These nonoxidizable cobalt species are suspected to be cobalt aluminate species (17, 30), which may possess some acidity. The weak correlation may be caused by the fact that not all these species are accessible to gas-phase molecules, the uncertainty in the determination of the amount of nonoxidizable cobalt species, and the interpolation procedure used for obtaining the average rate.

## 5. CONCLUSIONS

The reductive amination of ethanol using ammonia is catalyzed by reduced cobalt metal and the activity of the ethanol conversion is proportional to the metal surface area. The carrier acts as a support for a dispersed and stable metal phase which catalyzes the conversion of ethanol. Maximum activity is achieved using supports which provide a high extent of reduction of the supported cobalt while maintaining metallic dispersion. For the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  it was shown that increasing the time of hydrogen reduction at  $500^\circ\text{C}$  increases the reduced metal surface area, whereas increasing the reduction temperature yields the highest metal surface area at ca.  $500^\circ\text{C}$  due to the counteractive effects of increasing extent of reduction and increasing sintering.



Although the ethanol conversion was proportional to the number of zerovalent cobalt atoms at the surface, the ammonia conversion and product selectivity at constant ethanol conversion varied. This indicates a secondary conversion of the nitrogen compounds without ethanol. The changes in selectivity and in ammonia conversion are not related to the metal particle size. The differences are most likely to be ascribed to the secondary conversion of the product amines on acidic sites on the support via disproportionation to yield monoethylamine. Unreduced cobalt species on the alumina support might create these acid sites, since the selectivity of monoethylamine relative to the selectivity of diethylamine increases with decreasing extent of reduction. This is concurrent with the observed bifunctionality in the reductive amination of diethylene glycol over supported nickel catalysts (14).

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