# EFFECT OF COMPONENTS OF BASED CATALYTIC SYSTEM
# ON REDUCTIVE CARBONYLATION OF NITROBENZENE

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*Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.*

A three component catalytic system consisting of (i) elemental sulfur or sulfur compounds ($CS_2$, $H_2S$, COS), (ii) an alkali methoxide or triethylamine, and (iii) vanadium(V) compounds ($V_2O_5$, $NH_4VO_3$) has been applied as catalyst for reductive carbonylation of nitrobenzene to methyl N-phenyl carbamate with carbon monoxide and methanol at a temperature of $423 \pm 2$ K and an initial carbon monoxide pressure of 10 – 14 MPa/298 K. The efficiency of sulfur compounds increased in the sequence S : $CS_2$ : $H_2S$ : COS = 1 : 1.6 : 7.9 : 13.8. Hydrogen sulfide decreased however the selectivity of the reaction to the carbamate and increased that to aniline. Formation of the latter amine is increased especially in the presence of water in the reaction mixture and of hydrogen in the synthesis gas above 40 vol.%. The efficiency of the bases decreased in the order $CH_3OK$ > $CH_3ONa$ = NaOH > $(C_2H_5)_3N$ and of vanadium compounds in the sequence $NH_4VO_3$ > $V_2O_5$. The catalyst system thus allows to effect the reductive carbonylation of aromatic nitro compounds in the absence of transition metal compounds.

Much attention has long been paid to development of novel catalysts or catalytic systems for reductive carbonylation of aromatic nitro compounds, either based on Group VIII transition metals[1 – 5] or Group VI elements[6,7]. In the preceding work we examined[6] reductive carbonylation of nitrobenzene with carbon monoxide in the presence of methanol to produce methyl N-phenyl carbamate (MPC) and aniline (as a side product) with the use of the S ($CS_2$)–$CH_3COONa$–$V_2O_5$ catalyst at 360 – 470 K. This system was further improved and simplified by us, especially by using alkali metal alkoxides, alkali metal hydroxides or triethylamine as the more efficient bases compared to sodium acetate, minimizing sulfur content on applying hydrogen sulfide and carbonyl sulfide. Comparison was also made of the effectiveness of $V_2O_5$ and $NH_4VO_3$. The results obtained are reported in the present work.

## EXPERIMENTAL

### Chemicals

Nitrobenzene (chemical purity) contained 0.03 wt.% water and methanol (p.a.) contained 0.25 wt.% water (both supplied by Lachema, Brno). Methanolic sodium or potassium methoxide solutions were prepared by dissolving the corresponding alkali metal in a given alcohol. Carbon monoxide contained 1.8 vol.% of hydrogen, 0.2 vol.% of oxygen, 0.8 vol.% of nitrogen, and 0.1 vol.% of carbon dioxide. Elemental sulfur (chemical purity) was used as a sublimed powder, carbon disulfide was prepared from sodium sulfide by the action of hydrochloric acid (99.2% purity). Triethylamine (chemical purity) was dried and contained 0.2 wt.% of water. Vanadium pentoxide and ammonium metavanadate were of chemical purity. Sodium and potassium hydroxides were used in per analysis quality.

### Reductive Carbonylation

The effect of components of the catalytic system was studied with the use of a rotating (180 r.p.m.) stainless steel autoclave (500 cm$^3$ volume) which was heated electrically. The temperature was maintained with the accuracy of ± 2 K. The autoclave was charged in general with 50 g of nitrobenzene, 99 g of methanol and with different amounts of sulfur or sulfur compounds, inorganic or organic bases, vanadium pentoxide or ammonium metavanadate. The initial carbon monoxide pressure in the vessel was 10 to 14 MPa. The experiments were made for a constant time, this being 4 h from the attainment of the required reaction temperature. The rate of reductive carbonylation of nitrobenzene was calculated from the decrease of the pressure under standard conditions. The rate constant was determined from the first-order equation[6] $k = (1/t) \ln [(p_0 - p_k) / (p_t - p_k)]$, where k is the rate constant in min$^{-1}$, $p_0$ is the initial pressure and $p_k$ and $p_t$ is the final pressure and the pressure at time $t$, respectively. The reaction products including MPC and aniline were analyzed by GLC[8 – 10]. The same method was used to analyze phenyl formamide (2.4 m × 3 mm i.d.; column packed with 5% silicone elastomer SE-30 on Chromaton N-AWDMCS, column temperature 100 °C, injection port temperature 220 °C) with the use of ethanol as a solvent and naphthalene as internal reference. The elution time of naphthalene was 179 s and of phenyl formamide 240 s. In addition to GLC[11] analysis, N,N'-diphenylurea was determined also by its isolation and by liquid chromatography.

## RESULTS AND DISCUSSION

The following discussion will be concerned especially with the reductive carbonylation of nitrobenzene as a model aromatic nitro compound with carbon monoxide and methanol (80 – 200 °C, 1 – 30 MPa) to give methyl N-phenyl carbamate (MPC) catalyzed by a three component system consisting of (i) elemental sulfur or sulfur compounds (CS$_2$, H$_2$S, COS), (ii) alkali metal hydroxide or methoxide or triethylamine, and (iii) vanadium(V) compounds (V$_2$O$_5$, NH$_4$VO$_3$) (Eq. (A)).

$$C_6H_5NO_2 + 3\ CO + CH_3OH \xrightarrow{\text{cat}} C_6H_5NHCOOCH_3 + 2\ CO_2 \qquad (A)$$
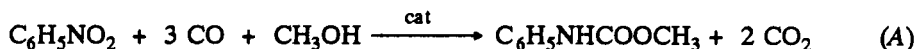
Figure 1 shows the dependence of the rate constant of the reductive carbonylation of nitrobenzene on the S/C$_6$H$_5$NO$_2$ molar ratio. The reaction was performed in methanol with the use of the S–CH$_3$ONa–V$_2$O$_5$ system at initial carbon monoxide pressure of 14

MPa (298 K). The increase of the rate constant with the increasing $S/C_6H_5NO_2$ molar ratio is evident. However, we deal here with rather high amounts of sulfur. This led us to carry out a series of constant time experiments (4 h) in which the effect of different amounts of sulfur or sulfur compounds on the conversion of nitrobenzene ($X$, in wt.%) and the selectivity ($S$, in wt.%) of the reductive carbonylation was determined at constant content of the base ($CH_3ONa$) and the vanadium component ($V_2O_5$). Reaction conditions and the results obtained are given in Table I. Figure 1 demonstrates the effect of the amount and type of sulfur (sulfur compound) on the rate constant $k$ ($min^{-1}$) of the studied reductive carbonylation. It is seen that of the sulfur compounds, the most efficient sulfur-containing component is carbonyl sulfide, followed by hydrogen sulfide, carbon disulfide, the least efficient being sulfur powder. When, under given reaction conditions, the efficiency of the sulfur compounds is related to the sulfur itself, one obtains the following sequence: $S : CS_2 : H_2S : COS = 1 : 1.6 : 7.9 : 13.8$. However, from the standpoint of the selectivity of the reductive carbonylation of nitrobenzene to MPC (Eq. (A)) or $C_6H_5NH_2$ (Eq. (B)), there exists a marked effect of hydrogen sulfide

$$C_6H_5NO_2 + 3\,CO + H_2O \rightarrow C_6H_5NH_2 + 3\,CO_2 \qquad (B)$$

respectively

$$C_6H_5NO_2 + 3\,CO + H_2S \rightarrow C_6H_5NH_2 + 2\,CO_2 + COS. \qquad (C)$$
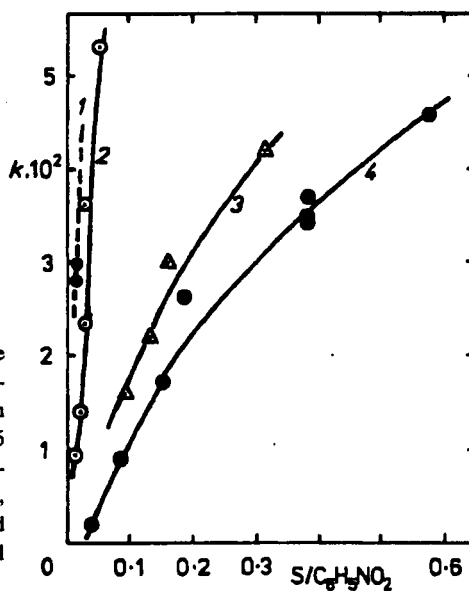


FIG. 1
Dependence of the rate constant $k$ (in $min^{-1}$) of the first-order kinetic equation of the reductive carbonylation of nitrobenzene (Eq. (A)) at $423 \pm 2$ K on $S/C_6H_5NO_2$ molar ratio. Conditions: 50 g (0.406 mol) nitrobenzene, 99 g (3 mol) methanol, the catalyst $S$–$CH_3ONa$–$V_2O_5$ (1 g $CH_3ONa$, 0.05 g $V_2O_5$), the pressure $p(CO)_0 = 14$ MPa (298 K). Sulfur added in the form of 1 COS, 2 $H_2S$, 3 $CS_2$, 4 elemental sulfur

While elemental sulfur, carbon disulfide or carbonyl sulfide all, when dry, do not affect significantly the selectivity of MPC formation, the highly efficient hydrogen sulfide brings about the increase of the selectivity to aniline formation on the expense of MPC formation. This decrease in MPC selectivity is detectable already on using

TABLE I
Effect of sulfur and sulfur compounds on nitrobenzene conversion ($X$, %) and selectivity ($S$, %) of the reductive carbonylation of nitrobenzene (4 h, reaction temperature 423 ± 2 K, $p(CO)_0$ = 14 MPa/298 K; charge: 50 g nitrobenzene, 99 g methanol, 1 g sodium methoxide, 0.05 g ammonium metavanadate, $x$ mol of sulfur or sulfur compound)

| Component | | | $X$ | $S$ to | |
| --- | --- | --- | --- | --- | --- |
| Type | mol S . $10^2$ | wt.%[a] | | MCP | $C_6H_5NH_2$ |
| None | – | – | 1.8 | 27 | 73 |
| S | 1.6 | 1 | 11.4 | 44.4 | 44.3 |
| | 3.1 | 2 | 17.3 | 50.9 | 43.0 |
| | 4.7 | 3 | 44.4 | 54.3 | 38.4 |
| | 6.2 | 4 | 64.3 | 77.2 | 9.8 |
| | 7.8 | 5 | 100 | 87.2 | 5.0 |
| | 15.6 | 10 | 100 | 89.1 | 6.0 |
| | 15.6 | 10 | 100 | 90.8 | 3.3 |
| | 15.6 | 10 | 100 | 92.2 | 2.5 |
| | 23.4 | 15 | 100 | 90.2 | 4.6 |
| None | – | – | 2.6 | 23.5 | 63.6 |
| $CS_2$ | 4.0 | 3 | 20.9 | 36.7 | 39.4 |
| | 5.3 | 4 | 73.6 | 85.4 | 7.1 |
| | 6.6 | 5 | 100 | 87.4 | 5.7 |
| | 13.1 | 10 | 100 | 89.2 | 6.3 |
| $H_2S$ | 0.2 | 0.1 | 8.4 | 19.8 | 79.5 |
| | 0.3 | 0.2 | 51.8 | 86.3 | 8.5 |
| | 0.4 | 0.3 | 89.3 | 82.2 | 12.7 |
| | 0.9 | 0.6 | 100 | 75.1 | 19.3 |
| | 1.0 | 0.7 | 100 | 74.6 | 23.1 |
| | 1.3 | 0.9 | 100 | 64.9 | 27.9 |
| | 2.1 | 1.4 | 100 | 53.6 | 42.1 |
| | 4.4 | 3.0 | 100 | 45.4 | 44.7 |
| | 12.0 | 8.8 | 100 | 3.9 | 96.0 |
| | 17.2 | 11.7 | 100 | 1.5 | 97.6 |
| COS | 0.6 | 0.71 | 100 | 84.8 | 7.5 |
| | 0.7 | 0.89 | 100 | 85.1 | 7.9 |

[a] With respect to nitrobenzene.

hydrogen sulfide at amounts above 0.3 wt.% with respect to nitrobenzene. The low selectivities of the reaction to MPC at low nitrobenzene conversions result mainly from the effect of water as an admixture of the starting compounds by reaction $(B)$. As far as the synthesis of the alkyl N-phenyl carbamate is concerned, the most efficient sulfur compound is carbonyl sulfide which, when compared to elemental sulfur, brings about the same reaction rate at the amount by one order of magnitude lower. This finding is also of practical importance as it shows that the synthesis can be carried out with the use of practically unpurified carbon monoxide[12].

The results obtained with carbonyl sulfide stress its role in the mechanism of the reductive carbonylation of aromatic nitro compounds. Its effect has been noticed also by Harper[13] who prepared N-phenyl carbamate from aniline via N,N'-diphenylurea in alkanol solution.

$$C_6H_5NH_2 + COS \rightarrow (C_6H_5NH)_2CO + H_2S$$

$$(C_6H_5NH)_2CO + ROH \rightarrow C_6H_5NH_2 + C_6H_5NHCOOR$$
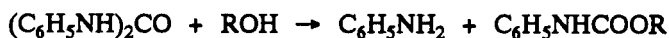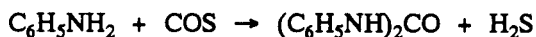
One cannot exclude the possibility that the insertion of CO to the presumed complex of the catalyst with nitrene[6] and likely also the formation of nitrene as the intermediate product of MPC by the reduction of the nitro group proceed easier with COS compared to CO.

$$C_6H_5NO_2 + 2\,COS \xrightarrow{\text{cat}} [\text{cat}-C_6H_5N:] + 2\,CO_2 + S$$
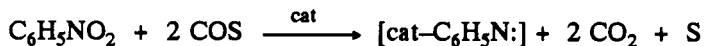
As side reactions lead to aniline, another reaction product can be also N,N'-diphenylurea[3,14].

$$C_6H_5NO_2 + C_6H_5NH_2 + 3\,CO \rightarrow C_6H_5NHCONHC_6H_5 + 2\,CO_2 \quad (D)$$

Furthermore, uncatalyzed carbonylation of organic compounds containing NH$_2$ or NH groups[15] can take place, giving phenylformamide.

$$C_6H_5NH_2 + CO \rightarrow C_6H_5NHCOH$$
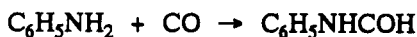
The presence of the above two compounds, that of N,N′-diphenylurea in greater amounts, in the products at nitrobenzene conversion above 50% has been established. These compounds thus form the residual part to 100% selectivity. As a rule, also methyl formate is present, which does not affect, however the above selectivity values.

The marked reductive effect of hydrogen present in hydrogen sulfide, leading to aniline formation (Eq. (*C*)), has led us to investigate the effect of hydrogen in carbon monoxide on the selectivity of the reductive carbonylation (Table II). The results obtained show that the selectivity is not decreased by hydrogen contents in carbon monoxide up to 15 vol.% and the selectivity changes are observable only at the hydrogen contents exceeding 40 vol.%. This indicates that the catalyst system activates only to small degree molecular hydrogen for the reduction of nitrobenzene. By contrast, water, similarly to the results of our previous work[6], affects significantly the selectivity of the reductive carbonylation, as shown in Table III.

When compared to the results of our previous work[6] where the function of the second component was fulfilled by sodium acetate, nearly by one order of magnitude greater effect on the reaction rate is exhibited by sodium methoxide. Well comparable to its action is also the action of sodium hydroxide (curve *2* in Fig. 2), the even stronger effect being demonstrated in the case of potassium methoxide (the stronger base) which further leads to the highest selectivity to MPC (Table IV). Triethylamine, as the weaker base, exerts considerably smaller effect on reaction rate (Table V and curve *3* in Fig. 2), its advantage being in simple regeneration from the reaction product. On the other hand, the disadvantage of the cheap and readily available sodium hydroxide is its lower

TABLE II
Effect of initial content of hydrogen ($H_2$ content in vol.%) in carbon monoxide on selectivity (*S*, %) of the reductive carbonylation of nitrobenzene (4 h, 423 ± 2 K; charge: 50 g $C_6H_5NO_2$, 99 g $CH_3OH$, 5 g S, 1 g $CH_3ONa$, 0.1 g $NH_4VO_3$)

| $P_{tot}^a$ | $H_2$ content | $S^b$ with respect to | |
|---|---|---|---|
| | | MPC | $C_6H_5NH_2$ |
| 14 | 1.8 | 84.8 | 8.3 |
| 14 | 5.3 | 85.7 | 10.0 |
| 14 | 15.8 | 86.4 | 6.6 |
| 14 | 15.8 | 84.3 | 8.3 |
| 16 | 44.8 | 73.8 | 24.6 |
| 16 | 50.9 | 53.9 | 46.1 |

[a] $P_{tot}$ denotes the total initial pressure (MPa/298 K); [b] the selectivity at 100% conversion of nitrobenzene.

selectivity to MPC which results from its in situ reaction with methanol to sodium methoxide, releasing reaction water.

It is worthy of mentioning that in case that the aim of the synthesis is formation of aniline or another aromatic amine, the preferred components of such a catalytic system could be hydrogen sulfide and alkali metal hydroxide. As shown above, formation of alkyl N-phenylcarbamates should be affected with aprotic base so as to supress the reaction of the base with the reactant (cf. Eq. (D)).

The third component of the catalytic system is vanadium(V) compound. Although the reductive carbonylation takes place even in the absence of a vanadium component, its rate is too slow (cf. reference experiment in Table VI with S–$CH_3ONa$ system). As expected, the promotion effect of V(V) compound increases with its increasing solubility in the reaction medium. Thus, for example the effect of ammonium metavanadate

TABLE III
Effect of water on selectivity (S, %) of the reductive carbonylation of nitrobenzene (4 h, 423 ± 2 K, $p(CO)_0$ = 14 MPa/298 K; charge: except for methanol the same as in Table II)

| $CH_3OH$ g/mol | $H_2O$ g/mol | $H_2O/CH_3OH$ molar ratio | X, %[a] | S with respect to | |
|---|---|---|---|---|---|
| | | | | MPC | $C_6H_5NH_2$ |
| 99/3.09 | 5/0.28 | 0.69 | 73 | 11.2 | 72.2 |
| 84/2.59 | 15/0.83 | 2.05 | 87 | 0.8 | 88.8 |
| 74/2.31 | 25/1.39 | 3.42 | 83 | 0.6 | 93.0 |
| 99/3.09 | 25/1.39 | 3.42 | 100 | 0.6 | 95.0 |
| 99/3.09 | 50/2.78 | 6.84 | 100 | 0 | 100.0 |
| 49/1.53 | 50/2.88 | 6.84 | 100 | 0.6 | 95.6 |

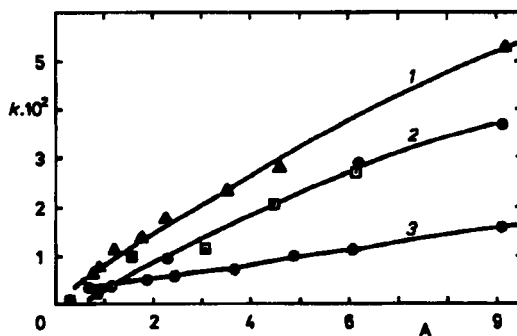[a] X is the nitrobenzene conversion.



FIG. 2
Effect of the base to nitrobenzene molar ratio (A) and of various bases on the rate constant k ($min^{-1}$) of the reductive carbonylation of nitrobenzene (see Table IV). 1 $CH_3OK$, 2 $CH_3ONa$ (circles) and NaOH (squares), 3 $(C_2H_5)_3N$

is three times greater than that of vanadium pentoxide. At the same time, vanadium(V) compounds do not affect the selectivity of the reductive carbonylation.

TABLE IV
Effect of alkali metal alkoxides and hydroxides on the conversion ($X$, %), rate constant ($k$, min$^{-1}$) and selectivity ($S$, %) of the reductive carbonylation of nitrobenzene (4 h, 423 ± 2 K, $p(CO)_0$ = 14 MPa/298 K; charge: 50 g $C_6H_5NO_2$, 100 g $CH_3OH$, 5 g S, 0.1 g $NH_4VO_3$)

| Component | | | $X$ | $k \cdot 10^2$ | $S$ with respect to | |
| --- | --- | --- | --- | --- | --- | --- |
| Type | wt.%[a] | base/$C_6H_5NO_2 \cdot 10^2$ molar ratio | | | MCP | $C_6H_5NH_2$ |
| None | – | – | 8.2 | – | 51.3 | 43.1 |
| $CH_3ONa$ | 0.01 | 0.02 | 15.5 | – | 40 | 60 |
| | 0.4 | 0.91 | 100 | 0.23 | 90.5 | 4.6 |
| | 0.5 | 1.14 | 98.9 | 0.38 | 90.8 | 4.1 |
| | 1.0 | 2.28 | 99.5 | 0.97 | 88.3 | 3.5 |
| | 2.0 | 4.55 | 100 | 2.91 | 85.4 | 7.8 |
| | 4.0 | 9.11 | 100 | 3.73 | 86.5 | 7.5 |
| $CH_3OK$ | 0.05 | 0.09 | 1.7 | – | 47.5 | 46.8 |
| | 0.5 | 0.88 | 84.9 | 0.64 | 90.8 | 1.0 |
| | 0.52 | 0.91 | 92 | 0.72 | 92.5 | 1.1 |
| | 0.65 | 1.14 | 98.6 | 1.18 | 92.2 | 2.5 |
| | 1.0 | 1.86 | 99.1 | 1.49 | 89.0 | 3.0 |
| | 1.3 | 2.28 | 100 | 1.76 | 89.0 | 2.6 |
| | 2.0 | 3.51 | 98.3 | 2.33 | 92.8 | 3.7 |
| | 2.6 | 4.56 | 100 | 2.82 | 93.7 | 5.8 |
| | 5.2 | 9.13 | 99.9 | 5.32 | 90.4 | 8.2 |
| NaOH | 0.1 | 0.31 | 74.3 | 0.07 | 83.4 | 3.0 |
| | 0.5 | 1.54 | 89.2 | 0.96 | 80.8 | 5.8 |
| | 1.0 | 3.08 | 100 | 1.16 | 84.4 | 9.2 |
| | 1.45 | 4.46 | 100 | 2.01 | 84.9 | 8.9 |
| | 2.0 | 6.16 | 100 | 2.71 | 83.5 | 10.7 |
| | 5.0 | 15.4 | 100 | 6.69 | 72.1 | 16.5 |
| | 10.0 | 30.8 | 100 | 12.44 | 55.0 | 28.2 |

[a] With respect to nitrobenzene.

TABLE V
Effect of triethylamine on the conversion ($X$, %), rate constant ($k$, min$^{-1}$) and selectivity ($S$, %) of the reductive carbonylation of nitrobenzene (4 h, 423 ± 2 K, $p(CO)_0 \approx 14$ MPa/298 K; charge: 50 g $C_6H_5NO_2$, 100 g $CH_3OH$, 0.1 g $NH_4VO_3$, 5 g S)

| $(C_2H_5)_3N^a$ wt.% / mol | $(C_2H_5)_3N/C_6H_5NO_2 \cdot 10^2$ molar ratio | $X$ | $k \cdot 10^2$ | $S$ with respect to | |
|---|---|---|---|---|---|
| | | | | MPC | $C_6H_5NH_2$ |
| 0.5/0.25 | 0.61 | 19.8 | 0.44 | 69.7 | 16.9 |
| 1.5/0.74 | 1.83 | 42.3 | 0.53 | 81.2 | 2.1 |
| 2.0/0.99 | 2.43 | 69.8 | 0.57 | 88.2 | 6.1 |
| 3.0/1.48 | 3.66 | 95.8 | 0.74 | 84.3 | 7.6 |
| 4.0/1.97 | 4.87 | 100 | 1.06 | 88.5 | 9.1 |
| 5.0/2.47 | 6.09 | 100 | 1.17 | 84.8 | 6.3 |
| 7.5/3.71 | 9.13 | 100 | 1.59 | 84.2 | 8.1 |
| 20.0/9.88 | 24.34 | 100 | 5.40 | 80.1 | 10.5 |

$^a$ wt.% related to the amount of nitrobenzene.

TABLE VI
Effect of vanadium(V) compounds on the conversion ($X$, %), rate constant ($k$, min$^{-1}$) and selectivity ($S$, %) of the reductive carbonylation of nitrobenzene (for conditions see Table IV, the charge contained also 1 g of $CH_3ONa$)

| Vanadium(V) compound | | | $X$ | $k \cdot 10^2$ | $S$ with respect to | |
|---|---|---|---|---|---|---|
| Type | wt.%$^a$ | wt.% V $\cdot 10^{3,b}$ | | | MCP | $C_6H_5NH_2$ |
| None | – | – | 19.2 | – | 60.4 | 29.2 |
| $V_2O_5$ | 0.0005 | 0.28 | 38 | 0.29 | 78 | 7 |
| | 0.001 | 0.56 | 52.6 | 0.34 | 84.8 | 6.7 |
| | 0.03 | 16.8 | 99.5 | 0.74 | 84.9 | 6.5 |
| | 0.05 | 28 | 100 | 1.62 | 82.6 | 8.5 |
| | 0.07 | 39 | 100 | 2.22 | 86.1 | 5.4 |
| | 0.10 | 56 | 100 | 2.91 | 85.4 | 7.8 |
| | 0.20 | 112 | 100 | 3.90 | 83.8 | 10.6 |
| | 0.30 | 168 | 100 | – | 79.1 | 13.3 |
| $NH_4VO_3$ | 0.001 | 0.44 | 19.4 | – | 75.0 | 2.9 |
| | 0.01 | 4.35 | 75.3 | 0.63 | 73.8 | 6.5 |
| | 0.03 | 13.1 | 100 | 2.18 | 88.9 | 4.7 |
| | 0.05 | 21.8 | 100 | 4.74 | 85.8 | 14.3 |
| | 0.10 | 43.6 | 100 | – | 80.5 | 9.0 |
| | 1.00 | 436 | 100 | 5.37 | 83.1 | 9.1 |
| | 1.50 | 653.6 | 100 | 8.53 | 84.1 | 10.1 |
| | 1.70 | 740.7 | 100 | 11.41 | 83.7 | 9.8 |

$^a$ With respect to nitrobenzene; $^b$ the metal to nitrobenzene weight ratio.

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Translated by J. Hetflejš.