HYDROGENATION OF 3-(DIMETHYLAMINO)PROPIONITRILE OVER PALLADIUM CATALYSTS

Jiří KRUPKA[1],*, Josef PAŠEK and Markéta NAVRÁTILOVÁ[2]

Department of Organic Technology, Institute of Chemical Technology, Prague, Technická 5,
166 28 Prague 6, Czech Republic; e-mail: [1] jiri.krupka@vscht.cz, [2] mnavrati@eurnotes.sial.com

Hydrogenation of 3-(dimethylamino)propionitrile over palladium catalysts was studied. Besides the expected amines, *N,N,N′*-tetramethylpropane-1,3-diamine, *N,N*-dimethyl-*N′*-propyl-propane-1,3-diamine, and *N,N*-bis[3-(dimethylamino)propyl]propylamine were found. Reaction pathways of their formation were discussed. Effects of reaction conditions, type of catalyst, and addition of ammonia or an amine into the charge on the hydrogenation selectivity were studied.

Key words: Reductions; Hydrogenation; Nitriles; Amines; Heterogeneous catalysis; Palladium; 3-(Dimethylamino)propionitrile; Reaction mechanisms; Selectivity.

This study concentrates on hydrogenation of 3-(dimethylamino)propionitrile over palladium catalysts, which have the ability to promote hydrogenation to higher alkylated amines. The aim of this study is to compare the course of hydrogenation over palladium of this rather complex and thermally less stable aminonitrile with hydrogenations of simple aliphatic amines, which were extensively investigated by Rylander[1,2], Rylander and Kaplan[3,4], Friefelder[5], Greenfield[6] or Koubek *et al.*[7], and Kostova[8]. Rylander and Friefelder state that the amines formed are strongly adsorbed on the surface of palladium or platinum and that the adsorption strength grows from tertiary to primary amines. Addition of a primary amine to nitrile can poison the palladium catalyst while addition of a secondary amine promotes the tertiary amine formation.

Koubek *et al.*[7] found remarkable results studying nitrile hydrogenation over palladium catalyst: hydrogenation rate of nitriles over palladium catalysts progressively dropped with increased conversion and the reaction stopped before 100% conversion; the maximum conversion achieved depended on the catalyst amount and the solvent used. The authors, however, proved that the effects observed were not caused either by the catalyst poisons contained in initial compounds, or thermodynamic factors or

strong adsorption of products or of some reaction intermediates on the catalyst surface. Palladium catalysts for nitrile hydrogenation are very sensitive to conditions of their preparation. Reduction of the catalysts with hydrogen in gaseous phase caused their total deactivation for nitrile hydrogenation while their activity in the C=C bond hydrogenation remained intact. So, as yet non-specified forms of adsorbed hydrogen play an important role in nitrile hydrogenation. Their varying content in the catalyst is a probable cause of irreproducible activity values of laboratory-prepared Pd catalysts in nitrile hydrogenation. In the opinion of the authors, in the case of supported Pd catalysts, both hydrogenation and condensation reactions must occur at the palladium surface.

Another reason, why selective hydrogenation of 3-(dimethylamino)propionitrile (DMAPN) to secondary and tertiary amines was chosen as the study object, was the application potential of the reaction. The tertiary amine, tris[3-(dimethylamino)propyl]amine (TDMAPA), as well as the secondary amine, N,N-bis[3-(dimethylamino)propyl]amine (BDMAPA), are both important auxiliary substances for polyurethane foams[9,10] and DMAPN hydrogenation over palladium catalysts (Pd/Al$_2$O$_3$, Pd/Li-spinel) is one of possible ways of their synthesis[11]. Thus the knowledge of influencing the reaction selectivity also bears a technological significance.

The primary amine derived from DMAPN, 3-(dimethylamino)propylamine (DMAPA), is widely used in many industries (production of tensides, paper, textiles, polyurethane elastomers and paints, cosmetics, *etc.*). It is manufactured by DMAPN hydrogenation over catalysts preferring the primary amine formation (Ni, Co) and, usually, in the presence of ammonia to suppress the secondary amine formation[12–15].

Our preliminary experiments with DMAPN hydrogenation over Pd catalysts revealed that the hydrogenation products contain, besides the respective tertiary, secondary and primary amines, several other compounds in concentrations of the order of percents or tens of percents. In DMAPN hydrogenation over Ni and Co catalysts, the compounds different from the respective primary and secondary amines were found in amounts less than 1%. Therefore, the main goal of the study was to investigate the nature of side products formed in hydrogenation over Pd catalysts, to elucidate reaction pathways of their formation, and to produce a list of some of the factors that may influence the course of DMAPN hydrogenation over palladium catalysts and its selectivity.

EXPERIMENTAL

High-Pressure Apparatus and Experimental Method

The experiments were performed in a 250-ml high-pressure autoclave equipped with a magnetic stirrer, thermocouple well, degassing valve, manometer and a probe with needle valve for sampling.

The reactor was charged with the catalyst, nitrile, and, possibly, a solvent or some of the amines studied and flushed with hydrogen three times. In hydrogenations in the presence of ammonia, the closed reactor was cooled with ice to 0 °C and then a required amount of liquid ammonia added from a pressure bottle. Then the reactor was pressurised with hydrogen and heated to the temperature required while stirring. The moment when the reaction temperature was reached (3–5 min) was taken as the reaction onset. Pressure was maintained within the range ±0.5 MPa by addition of hydrogen from the cylinder. Liquid samples were withdrawn in regular intervals and analysed. Under the reaction conditions given, the rate of hydrogenation was not affected by internal or external mass transfers.

Analysis

Composition of samples was analysed by GLC using a non-polar capillary with silicone DB-5 (J&W Scientific), 0.53 mm in diameter and 30 m long, with the temperature programme 100 °C/3 min/10 °C min^{-1}/250 °C. The reaction mixture composition was determined by the method of internal normalisation and is given in weight percentage. Qualitative evidence for respective compounds was obtained with mass spectrographs GC-MS HP 6890 or GC-MS Varian Saturn 2000. The identity of some of the compounds was also confirmed by comparing their elution times with elution times of standards over several bonded stationary phases.

Chemicals

DMAPN (VÚOS Pardubice) was vacuum-distilled, GLC purity 99.9%. DMAPA (BASF) was column-distilled, GLC purity 99.98%. BDMAPA and TDMAPA were synthesised and column-distilled; their impurities were below 0.4%. Other chemicals used were of analytical grade.

Catalysts

List of the studied catalysts is given in Table I. All catalysts were used in a powder form.

RESULTS AND DISCUSSION

Composition of the Reaction Mixtures

In contrast to hydrogenation of lower aliphatic nitriles over Pd, where usually just a tertiary amine is present in the hydrogenation product, in DMAPN hydrogenation over Pd, the reaction products also contained the secondary amine in substantial amounts (Table II). This is to be accounted

Table I
Catalysts

Composition	Ref. code, manufacturer	Characteristics, notes
5 wt.%Pd/active C	CARBONOR NS Doduco	water content 52.1 wt.%[a]
0.56 wt.% Pd/Al$_2$O$_3$	CHEROX 4000 Chemopetrol Litvinov	total specific surface area 185 m^2/g
2 wt.% Pd/SiO$_2$/Al$_2$O$_3$	MGS-5 Montecatini	pellets with SiO$_2$ core and Al$_2$O$_3$ surface, impregnated with Pd
10 wt.% Pd/Al$_2$O$_3$	8874H Koch-Light	
5 wt.% Pd/Al$_2$O$_3$	K-0251 Heraeus	total specific surface area 150 m^2/g, Pd surface area 7.4 m^2/g
5 wt.% Pd/Al$_2$O$_3$	K-0250 Heraeus	total specific surface area 20 m^2/g, Pd surface area 6 m^2/g
5 wt.% Ru/Al$_2$O$_3$	ESCAT 44 Engelhard	total specific surface area 125 m^2/g
5 wt.% Pt/active C	SECOMET AN Doduco	water content 50 wt.%[a]
Pd-black		prepared according to ref.[16]
Aluminosilicate	SIRALOX 20/380 Condea Chemie	highly acidic

[a] The catalyst activities are relative to dry weight.

Table II
The course of 3-(dimethylamino)propionitrile hydrogenation over 5% Pd/Al$_2$O$_3$[a] (150 m^2/g$_{cat}$)

Compound	Reaction mixture composition, wt.%				
	0.25 h	0.5 h	1 h	2 h	4 h
DMA + TMA	0.19	0.13	0.03	0.01	0.01
PA	0.21	0.13	0.04	0.02	0.01
DMAPA	0.92	1.10	1.14	1.05	1.05
DMAPN	57.68	23.60	2.26	0.10	0.03
TMDAP	1.93	2.69	2.82	2.57	2.43
PDMAPA	0.60	0.63	0.68	0.62	0.61
BDMAPA	17.41	25.15	29.23	29.38	29.41
PBDMAPA	1.94	2.78	3.31	3.45	3.52
TDMAPA	18.50	43.17	60.12	62.60	62.75
Others	0.62	0.62	0.37	0.21	0.18

[a] 90 °C, 9 MPa, 74 g DMAPN, 2 g catalyst.

for by the steric effects. The primary amine concentration was low, rarely over 1%.

In addition to the nitrile and corresponding amines, other compounds were identified in reaction mixtures. Three of them were present in concentrations of the order of percents or tens of percents (Tables III–V). In some cases, their contents were higher than those of the main products (Table III). They were $N,N,N'N'$-tetramethylpropane-1,3-diamine (TMDAP), N,N-dimethyl-N'-propylpropane-1,3-diamine (PDMAPA), and N,N-bis[3-(dimethylamino)-propyl]propylamine (PBDMAPA). The cause of their formation should be sought in the DMAPN decomposition. DMAPN decomposes to yield dimethylamine and acrylonitrile, which is the reverse reaction to dimethylamine addition to acrylonitrile (Scheme 1).

TABLE III
Effect of the Pd catalyst type on selectivity of 3-(dimethylamino)propionitrile hydrogenation[a,b]

| Catalyst	0.56%Pd/Al$_2$O$_3$	5%Pd/C	2%Pd/SiO$_2$–Al$_2$O$_3$	Pd-black
Catalyst concentration[c]	2.73%	2.73%[d]	6.83%	2.70%
Sampling time	5 h	7 h	3 h	4 h
Nitrile conversion[e]	39.5%	42.5%	41.5%	19.5%
DMA + TMA	0.06	0.07	0.04	0.10
PA	0.06	0.05	0.02	0.13
DMAP	1.31	5.85	1.57	0.31
DMAPA	0.55	0.18	0.24	0.23
DMAPN	60.49	57.50	58.50	80.54
TMDAP	9.63	14.90	9.06	2.91
PDMAPA	1.44	0.78	0.55	0.64
BDMAPA	6.56	1.42	3.87	2.39
PBDMAPA	5.41	7.12	7.63	2.94
TDMAPA	12.01	5.54	15.43	9.11
Others	2.48	6.59	3.09	0.70
Max. conversion[f]	54%	42.5%	53%	19.5%

[a] 110 °C, 9 Mpa; [b] the values in the table are in wt.%; [c] relative to DMAPN; [d] concentration of the dry matter catalyst; [e] at which selectivity values were compared; [f] the reaction stopped at the given incomplete conversions.

$$H_3C \diagdown N-CH_2-CH_2-C\equiv N \rightleftharpoons H_3C \diagdown NH + CH_2=CH-C\equiv N$$
$$H_3C \diagup \qquad\qquad\qquad\qquad H_3C \diagup$$
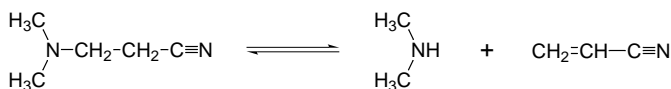
SCHEME 1

To explain the formation of final side products detected in reaction mixtures, the reaction scheme of nitriles hydrogenation based on modified Braun's mechanism[1,2,6,17] is used. Thus, the participation of imines and enamines as reactive intermediates in the formation of secondary and tertiary amines is assumed. However, the reaction pathways introduced below do not specify whether the imine intermediates desorb to the reaction mixture or exist only as adsorbed compounds on the catalyst surface.

Under the hydrogenation conditions, acrylonitrile yields propylideneamine and further propylamine (Scheme 2).

$$CH_2=CH-C\equiv N \xrightarrow{+H_2} CH_3-CH_2-C\equiv N \xrightarrow{+H_2} CH_3-CH_2-CH=NH \xrightarrow{+H_2} CH_3-CH_2-CH_2-NH_2$$
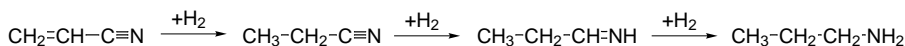
SCHEME 2

Dimethylamine and propylamine were found in reaction mixtures in very low concentrations (Tables II–V), which confirms that, over palladium, condensation reactions prevail over hydrogenation reactions. Thus the
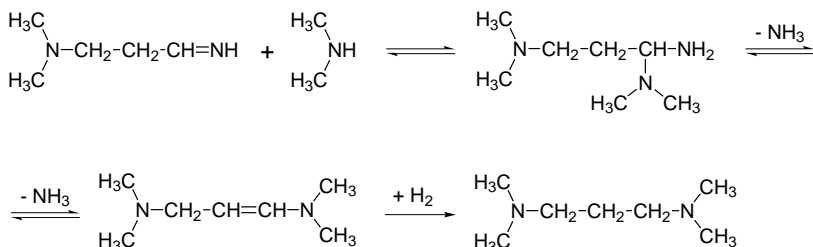
TABLE IV
Comparison of 2% $Pd/SiO_2–Al_2O_3$ and 5% Pd/Al_2O_3 (150 m^2/g_{cat}) catalysts in 3-(dimethylamino)propionitrile hydrogenation in the presence of 14 wt.% ammonia[a,b]

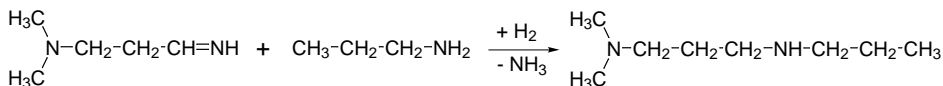| Catalyst	2%$Pd/SiO_2–Al_2O_3$	0.5%Pd/Al_2O_3(150m^2/g_{cat})
Catalyst concentration[c]	13.51%	5.41%
Sampling time	5 h	3 h
Nitrile conversion[e]	99.9%	99.9%
DMA + TMA	0.04	0.00
PA	0.06	0.01
DMAP	1.08	0.17
DMAPA	0.19	1.47
DMAPN	0.07	0.01
TMDAP	12.93	7.32
PDMAPA	1.98	2.09
BDMAPA	9.72	24.56
PBDMAPA	15.1	8.46
TDMAPA	56.18	54.1
Others	2.65	1.81

[a] 110 °C, 7 Mpa; [b] the values in the table are in wt.%; [c] relative to DMAPN.

dimethylamine and propylamine formed do not remain in the reaction mixture but undergo further reactions. Dimethylamine reacts with aldimine intermediate, [3-(dimethylamino)propylidene]amine, yielding TMDAP in subsequent reactions (Scheme 3).

$$H_3C-N-CH_2-CH_2-CH=NH \quad + \quad H_3C-NH \quad \rightleftharpoons \quad H_3C-N-CH_2-CH_2-CH-NH_2 \quad \xrightarrow{- NH_3}$$

$$\xrightarrow{- NH_3} \quad H_3C-N-CH_2-CH=CH-N-CH_3 \quad \xrightarrow{+ H_2} \quad H_3C-N-CH_2-CH_2-CH_2-N-CH_3$$

SCHEME 3

In a similar way, propylamine is converted into PDMAPA (Scheme 4).

$$H_3C-N-CH_2-CH_2-CH=NH \quad + \quad CH_3-CH_2-CH_2-NH_2 \quad \xrightarrow[- NH_3]{+ H_2} \quad H_3C-N-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_3$$

SCHEME 4

The PDMAPA formed can be added to the aldimine to give PBDMAPA. Another possible pathway to PDMAPA and PBDMAPA is the addition of primary amine, DMAPA, or secondary amine, BDMAPA, to propylideneamine. By analogy (see Scheme 5), dimethylamine and propylideneamine form *N,N*-methylpropylamine (DMAP), which was also detected in some reaction mixtures (Tables III–V).

$$H_3C-NH \quad + \quad CH_3-CH_2-CH=NH \quad \xrightarrow[- NH_3]{+ H_2} \quad H_3C-N-CH_2-CH_2-CH_3$$
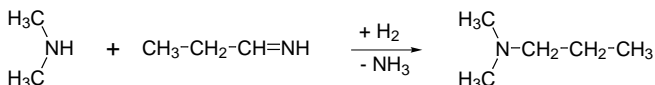
SCHEME 5

The primary or secondary amine may also add onto the C=C bond in acrylonitrile. As follows from the mass balance, however, virtually all acrylonitrile was converted to propylamino groups, and if addition to C=C bond occurred, then to a negligible extent. It can be concluded that the hydrogenation rate of the polarised C=C bond in acrylonitrile is much higher than that of amine addition to the C=C bond.

Relatively high concentrations of compounds TMDAP, PDMAPA and PBDMAPA were present in the reaction mixtures catalysed with both supported Pd catalysts and palladium black. It was found that under the reac-

tion conditions given (90–110 °C, 9 MPa), there is virtually no thermal decomposition of the nitrile in the homogeneous phase if no catalyst is present. In hydrogenation of DMAPN over Ni and Co catalysts, the content of compounds originating from the nitrile decomposition is also low[18]. It is obvious that DMAPN decomposition is catalysed by palladium. We guess that the reason is the extraordinary property of palladium to behave in some situations in the presence of hydrogen as an acid catalyst[19,20]. According to Červený and Růžička[19], acid properties of the Pd–H system are caused by the protonic character of the hydrogen activated by palladium. It was also found in our study that an addition of an acid aluminosilicate to the Pd catalyst (20% of aluminosilicate per Pd/SiO_2–Al_2O_3) increased the extent of the reactions based on DMAPN decomposition (from 17 to 24%). This fact supports the idea that DMAPN decomposition occurs due to the acid properties of the Pd–H system.

TABLE V
Comparison of 5% Pd/Al_2O_3 and 10% Pd/Al_2O_3 catalysts in hydrogenation of 3-(dimethyl-amino)propionitrile in the presence of 20 wt.% ammonia[a,b]

Catalyst	5%Pd/Al_2O_3	5%Pd/Al_2O_3	10%Pd/Al_2O_3
Total spec. surf. area	(150 m^2/g_{cat})	(20 m^2/g_{cat})	
Catalyst concentration[c]	2.70%	2.70%	2.70%
Sampling time	1 h	3 h	1 h
Nitrile conversion[e]	91.2%	91.8%	89.0%
DMA + TMA	0.01	0.01	0.10
PA	0.02	0.02	0.07
DMAP	0.00	0.01	0.04
DMAPA	3.38	3.34	1.85
DMAPN	8.86	8.16	11.00
TMDAP	1.23	1.62	1.51
PDMAPA	0.63	0.72	0.64
BDMAPA	45.33	39.00	34.74
PBDMAPA	1.03	1.61	1.64
TDMAPA	38.12	44.4	47.42
Others	1.39	1.11	0.99
Max. conversion[e]	100%	100%	100%

[a] 90 °C, 9 Mpa; [b] the values in the table are in wt.%; [c] relative to DMAPN; [d] at which selectivity values were compared; [e] maximum conversion achieved.

The discussed acidity of the Pd–H system causes that in DMAPN hydrogenation over Pd catalysts, the yield of the desired amines, BDMAPA and TDMAPA, can reach 92% as a maximum. For comparison, if Ni and Co catalysts are employed, the DMAPA and BDMAPA yields commonly achieved are above 99%.

Selectivity and Activity of Palladium Catalysts

The influence of the Pd catalyst type and reaction conditions on the course of DMAPN hydrogenation were followed in more than 60 experiments. Only selected experiments are given in Tables II–VII.

The DMAPN hydrogenation was studied over palladium black and palladium catalysts differing in their supports (active C, Al_2O_3, SiO_2–Al_2O_3), surface areas (20 or 150 m^2/g_{cat}) or palladium contents (0.56, 5, and 10 wt.% Pd/Al_2O_3, respectively). The selectivity values were always compared for the reaction mixtures having the same degrees of conversion. The catalysts were mostly tested under the following conditions: batch hydrogenation without solvent, reaction pressure 9 MPa, reaction temperature 110 or 90 °C, and catalyst concentration 1–10 $g_{cat}/74$ g DMAPN depending on the catalyst activity. The catalyst properties were also tested in the nitrile hydrogenation with ammonia added to the charge.

TABLE VI
Effect of ammonia on selectivity of 3-(dimethylamino)propionitrile hydrogenation catalysed with 2% Pd/SiO_2–Al_2O_3[a]

NH$_3$ concentration[b]	0%	14%	25%	33%
Nitrile conversion	99.9%	99.9%	99.9%	99.1%
DMAPA	0.08	0.19	2.82	4.15
DMAPN	0.09	0.07	0.03	0.84
TMDAP	16.18	12.93	6.16	6.93
PDMAPA	1.67	1.98	2.94	3.54
BDMAPA	5.73	9.72	41.90	46.50
PBDMAPA	18.90	15.10	5.26	4.46
TDMAPA	45.70	56.18	38.10	30.70
Others	11.65	3.87	2.79	2.88

[a] 110 °C, 7 MPa, 13.51% of catalyst relative to DMAPN, constant total pressure; [b] relative to the sum DMAPN + NH$_3$.

The course of DMAPN hydrogenation over Pd catalysts had low reproducibility in comparison with that over Ni or Co. Therefore only relative ranking of catalysts according to their activity and selectivity is given.

It was found that DMAPN hydrogenation rate decreased with growing nitrile conversion; with catalysts of lower activity, the reaction stopped at incomplete conversion under certain reaction conditions. In hydrogenations of simple aliphatic nitriles[7], similar conclusions were made.

The activity of the catalysts was compared on the basis of the reaction time required for 20% conversion of the nitrile. The order of growing hydrogenation activity of the catalysts at a constant palladium concentration in the reaction mixture is: Pd-black << 5% Pd/C < 2% Pd/SiO$_2$–Al$_2$O$_3$ < 0.56% Pd/Al$_2$O$_3$ < 5% Pd/Al$_2$O$_3$ (20 m^2/g$_{cat}$) < 10% Pd/Al$_2$O$_3$ < 5% Pd/Al$_2$O$_3$ (150 m^2/g$_{cat}$). The 5% Pd/Al$_2$O$_3$ catalyst possesses a significantly higher activity than the 5% Pd/C.

Based on the maximum achieved total conversion of the nitrile, the catalysts may be classified into three groups. The achieved conversion is tenaciously dependent on the catalyst activity. The first two catalysts of the lowest activity in the sequence did not give full conversion even at high Pd concentrations in the reaction mixture. In contrast, the full conversion of 100% was obtained with the three most active catalysts even at a low con-

TABLE VII
Hydrogenation of 3-(dimethylamino)propionitrile in the presence of added amine[a,b]

Amine added Reaction time	DMAPA			BDMAPA			TDMAPA		
	0 h	2 h	4 h	0 h	2 h	4 h	0 h	2 h	4 h
DMAPA	50.99	11.90	10.60	–	0.67	0.66	–	0.65	0.51
DMAPN	49.01	2.74	0.07	34.39	5.19	1.17	28.01	1.01	0.02
TMDAP	–	0.33	0.35	–	1.07	1.20	–	1.03	0.84
PDMAPA	–	0.38	0.40	–	0.26	0.29	–	0.41	0.42
BDMAPA	–	79.17	82.16	65.61	56.83	55.88	–	14.60	14.51
PBDMAPA	–	0.06	0.07	–	1.49	1.66	–	0.69	0.74
TDMAPA	–	4.97	5.68	–	34.20	38.89	71.99	81.34	82.73
Others	–	0.45	0.67	–	0.29	0.25	–	0.27	0.23

[a] 90 °C, 9 MPa, 1 g of 5% Pd/Al$_2$O$_3$ (150 m^2/g$_{cat}$), 37 g DMAPN, molar ratio amine/nitrile 1 : 1; [b] for the reaction in the absence of added amine, see Table II.

centrations of 0.1% Pd (relative to the nitrile). The two remaining catalysts are medium-activity samples, which gave 100% conversion only at substantially higher Pd concentrations.

From the experiments where 100% conversion was achieved, the time dependence of the nitrile concentration was evaluated by a simple kinetic equation $r = k\, c_{DMAPN}^n$. The formal reaction order with respect to nitrile varied in experiments in the range $n = 0.6$–1.3. In hydrogenation of lower linear nitriles over Pd, Koubek et al.[7] found $n = 1.0$–1.3. In hydrogenation of simple nitriles over cobalt and nickel catalysts, the formal order of reaction was found[7,8] to be $n = 0$–0.6. The relatively high order of reaction over Pd indicates somewhat stronger adsorption of the products on palladium as compared with that of Co or Ni.

Catalyst selectivity may be evaluated either from the viewpoint of the ratio of the main products, BDMAPA and TDMAPA, or from the viewpoint of the total yield of the main products, which is naturally given by the side product content, i.e., TMDAP, PDMAPA, and PBDMAPA. The TDMAPA/BDMAPA ratio does not depend much on the type of Pd catalyst. Selectivity to main products, i.e., the total yield of BDMAPA and TDMAPA, decreases, due to side reactions, as follows: 10% $Pd/Al_2O_3 \approx 5\%$ Pd/Al_2O_3 (150 m^2/g_{cat}) > 5% Pd/Al_2O_3 (20 m^2/g_{cat}) > Pd-black > 0.56% $Pd/Al_2O_3 \approx 2\%$ Pd/SiO_2–Al_2O_3 > 5% Pd/C.

By comparing the hydrogenation activity series of the catalysts with the selectivity series, the following points are revealed:

1. Except for palladium black, the more active is the catalyst, the fewer side products are formed. It seems that different active centres on the catalyst surface participate in DMAPN hydrogenation and in its decomposition.

2. Palladium black has the lowest hydrogenation activity and, at the same time, medium selectivity to the main products. This suggests that, besides Pd, also the supports partially contribute to the DMAPN decomposition.

3. From the viewpoint of selectivity and activity in DMAPN hydrogenation, active carbon is not suitable as a Pd support.

Activity and selectivity of 5% Pt/C and 5% Ru/Al_2O_3 (125 m^2/g_{cat}) catalysts were also tested in the hydrogenation. Compared with all the catalysts tested, 5% Ru/Al_2O_3 exhibited the lowest activity; the primary amine DMAPA was the main product. The 5% Pt/C catalyst showed a comparable activity to that of the 5% Pd/C catalyst; DMAPA was also the main product. The contents of side products originating from the nitrile decomposition in hydrogenation runs over Pt and Ru catalysts were lower than those obtained over corresponding palladium catalysts. It follows from the results

that the high activity for the DMAPN decomposition is obviously character-
istic of palladium only.

Effect of Ammonia and Amine on Hydrogenation of 3-(Dimethylamino)propionitrile

Ammonia addition increased the selectivity to main products, which may
lead to the conclusion that ammonia inhibits the DMAPN decomposition
(Table VI). The ammonia effect on selectivity is the more pronounced the
lower is the catalyst activity. If a less active catalyst, *e.g.*, 2% $Pd/SiO_2-Al_2O_3$,
was used, the hydrogenate (90 °C, 9 MPa) contained 28% of side products
when no ammonia was added; in the presence of 20 wt.% of ammonia, only
7% of side products was formed. With a more active 5% Pd/Al_2O_3 (150 m^2/g_{cat})
catalyst, ammonia addition decreased the impurities contents from 6.8 to
4.8%. The experiments mentioned are not given in tables where, however,
similar results can be seen.

The ammonia concentration has little effect on the hydrogenation rate if
a constant partial pressure of hydrogen is maintained. As the ammonia
amount added increases, the TDMAPA/BDMAPA ratio decreases, which co-
incides with the reaction scheme[17] of nitrile hydrogenation.

The positive effect of ammonia on the DMAPN hydrogenation selectivity
is also supported by the experimental observations that in hydrogenation
with no ammonia added, selectivity increases with the growing nitrile con-
version because the ammonia formed is accumulated in the reaction mix-
ture. The inhibiting effect of ammonia on the DMAPN decomposition is
not explained.

The effects of additions of the primary, secondary, and tertiary amines on
the course of the DMAPN hydrogenation were also investigated (Table VII).
Addition of a primary amine to the nitrile increased the yield of the second-
ary amine, the finding being in accordance with data provided by the
Bayers' patent[11]. If BDMAPA was added, almost all DMAPN was converted
to TDMAPA. It follows from the results that the presence of primary, sec-
ondary, or tertiary amines in the charge causes a decrease in the DMAPN
hydrogenation rate.

Effect of Reaction Conditions on Hydrogenation of 3-(Dimethylamino)propionitrile

According to literature[2,3,7,21], the type and amount of solvent have substan-
tial effects on the reaction rate and selectivity of hydrogenation over plati-

num metals. In most experiments, DMAPN was hydrogenated without any solvent; however, hydrogenation in methanol or in *tert*-butyl methyl ether was also tested. In the batchmode, at the molar ratio solvent/DMAPN = 1, neither *tert*-butyl methyl ether nor methanol showed any effects on the reaction rate and selectivity of the hydrogenation.

It was found in the pressure range from 6 to 10 MPa that a high hydrogen pressure somewhat reduced the ratio of the tertiary to secondary amine in accord with the concept that with increasing pressure hydrogenation reactions are preferred at the expense of condensation ones. In fact, the pressure effects are much more complex because there are cases described in literature when with growing pressure, compositions changed towards higher contents of higher amines[17]. It was found in the study that in DMAPN hydrogenation, the ratio of tertiary to secondary amine in products was higher at 90 than of 110 °C. The ratio also grows with decreasing catalyst amount. The content of side products increases with reaction temperature and with decreasing hydrogen pressure.

The ratio of the tertiary to secondary amine can be increased by an addition of an acid aluminosilicate to the reaction mixture (from 0.9 to 1.3 by addition of 20% of aluminosilicate per Pd/SiO$_2$–Al$_2$O$_3$ catalyst); at the same time, the side product formation increases and thus the total content of main products is reduced. The fact that the aluminosilicate presence in the reaction mixture increases the ratio of the tertiary to secondary amine indicates that the condensation reactions need not occur only on the surface of the palladium catalyst.

CONCLUSION

The formation of secondary and tertiary amines is preferred in the hydrogenation of 3-(dimethylamino)propionitrile over palladium. The addition of the primary amine to the nitrile charge can be employed for selective synthesis of the secondary amine. In a similar way, addition of the secondary amine, or its recycling, has a consequence of almost quantitative nitrile conversion to the tertiary amine.

In the hydrogenation of 3-(dimethylamino)propionitrile, palladium catalyses not merely the hydrogenation reaction, but also the nitrile decomposition. *N,N,N'N'*-Tetramethylpropane-1,3-diamine, *N,N*-dimethyl-*N'*-propyl-propane-1,3-diamine, and *N,N*-bis[3-(dimethylamino)propyl]propylamine are the final products of the nitrile decomposition. The lower is the hydrogenation activity of the palladium catalysts supported, the higher is the extent of the nitrile decomposition. Since the addition of aluminosilicate to

the Pd catalyst also increased the extent of side reactions, it is highly probable that the 3-(dimethylamino)propionitrile decomposition occurred due to the acid properties of the Pd–H system.

An ammonia addition to the hydrogenated nitrile substantially suppresses side product formation. The composition of side products demonstrated that the acrylonitrile formed in 3-(dimethylamino)propionitrile decomposition reacted to yield mostly *N*-propyl derivatives. An amine addition to the C=C bond in acrylonitrile is very low. So, the reaction rate of C=C bond hydrogenation is higher than that of amine addition to the bond.

LIST OF SYMBOLS

BDMAPA	*N*,*N*-bis[3-(dimethylamino)propyl]amine
c	concentration (weight fraction)
DMA	dimethylamine
DMAP	*N*,*N*-dimethylpropylamine
DMAPA	3-(dimethylamino)propylamine
DMAPN	3-(dimethylamino)propionitrile
g_{cat}	gram of catalyst
k	reaction rate coefficient
m	mass
MA	methylamine
n	order of the reaction with respect to nitrile
PA	propylamine
PBDMAPA	*N*,*N*-bis[3-(dimethylamino)propyl]propylamine
PDMAPA	*N*,*N*-dimethyl-*N'*-propylpropane-1,3-diamine
r	reaction rate
TDMAPA	tris[3-(dimethylamino)propyl]amine
TMA	trimethylamine
TMDAP	*N*,*N*,*N'N'*-tetramethylpropane-1,3-diamine
wt.%	weight percentage

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