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Dedicated to Professor Valer Fărcăşan
at his 85th anniversary

CATALYTIC REDUCTIVE AMINATION OF BUTANAL OVER CARBON SUPPORTED NOBLE METALS

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ABSTRACT. The reductive amination of butanal with ammonia (at ammonia/butanal molar ratios of ~ 14.5) and hydrogen has been performed at 50 bar and 323-353 K over graphite and charcoal supported noble metal catalysts. Rhodium and platinum based catalysts showed the highest activity. The BET area and metal dispersion markedly influenced the activity without changing the selectivity. The products (butylamine, dibutylamine and tributylamine) were detected in the reaction mixture only after an apparent induction period. Butylamine and dibutylamine seem to be primary products, which are hardly interconverted. Good hydrogenolysis catalysts (Ru, Rh) produced mostly primary amines, while active hydrogenation catalysts (Pt, Pd) directed the reductive amination of butanal towards secondary and tertiary amines.

Keywords: Reductive amination, Butanal, Amines, Noble metal catalysts, Carbon supports

INTRODUCTION

The reductive amination of aldehydes and ketones with ammonia and hydrogen is an important synthetic route to amines and proceeds through an intermediately formed aminoalcohol [1]. This may be dehydrated to imine, which is subsequently hydrogenated or can be directly hydrogenolized to primary amine in presence of a catalyst. The primary amine formed can also behave as an aminating agent for the carbonyl compound forming a Schiff base, which is reduced to secondary amine [1]. The addition of a primary amine to the imine with subsequent reduction of the adduct also leads to secondary amine. The secondary amine can react similarly with the carbonyl compound or with the imine, forming tertiary amine. The principal side reaction is the hydrogenolysis reaction of the carbonyl compound involving the formation of the corresponding alcohol. Apparently, the formation of the primary amine should proceed only through aminoalcohol-imine intermediates, but there is evidence that secondary and tertiary amine precursors could be present at concentrations much higher than the amount of secondary and tertiary amine obtained at the end [2]. Thus, the reaction paths leading to the final product and, so, determining the selectivity of a particular catalyst under a set of reaction conditions are not clearly known.

There are numerous reports on the use of supported and unsupported Ni, Co and noble metal catalysts [1,3-11]. Metal sulfides (Re, Fe, Co, Ni, W, Pt, Rh) were also used [12-14] as catalysts in the reductive amination of ketones. The relative inactivity of these catalysts for the hydrogenation of the aromatic ring, ketones, nitriles, esters and other unsaturated functional groups, often permits useful selectivity in case of multifunctional compounds.

Butanal [15] was chosen as test molecule in this study because of lack of literature information concerning the reductive amination of this substrate with ammonia and hydrogen over supported noble metal catalysts.

EXPERIMENTAL

CATALYSTS: The catalysts tested in the reductive amination of butanal are presented in Table 1 together with some physicochemical characterization data as well. The charcoal supported catalysts contained 55-60% moisture. The quantitative values used for these samples refer to dry material.

Table 1

Catalysts characterization data (metal dispersions were calculated by using n_S values estimated according to literature [16])

Type of catalyst	S_{sp} (m^2/g)	S_M (m^2/g)	Metal location	Dispersion (%)	BET area (m^2/g)
5%Rh/charcoal	950	11.1	Intermediate	50.4	817.8
5%Rh/HSAgraphite	130	9.5	Surface	43.2	94.6
5%Ru/HSAgraphite.	130	8.0	Surface	43.8	41.6
5%Pd/charcoal	995	18.5	Intermediate	83.0	n.a.
5%Pd/HSAgraphite	130	11.4	Surface	51.1	87.6
5%Pt/HSAgraphite	130	5.0	Surface	40.5	80.1
5%Pt/LSAgraphite	n.a.	3.5	Surface	28.0	56.7

Ssp	specific surface area of the support
S_M	metal surface area determined by hydrogen chemisorption
HSA	high surface area
LSA	low surface area

CATALYSTS TESTING: The reactions were carried out in batch reactors with a volume of about 65 ml. Magnetic stirring at a speed of 1100 rpm was used. The temperature inside the autoclave was measured by a thermocouple mounted on the lid of the autoclave. Weighed amount of catalysts were introduced into the autoclave. In order to assure a well-defined starting time for every reaction, the following experimental procedure was applied: after addition of butanal (>99%, Merck) and of the solvent (ethanol), the autoclave was flushed with nitrogen to remove the atmospheric oxygen. Ammonia was then added from the liquid ammonia cylinder at room temperature. Then the autoclave was placed in a thermostat bath preset to the reaction temperature. Adding hydrogen and completing fast to the working pressure occurred only after the preformed imine solution reached the desired reaction temperature (t = 0 is set for the time when the final pressure was established).

The progress of reaction in time was evaluated from the hydrogen consumption by measuring the hydrogen flow with a flow meter (BROOKS) having the pressure inside the autoclave controlled by a pressure regulator (BROOKS). Liquid sampling was used for monitoring the evolution of products in time.

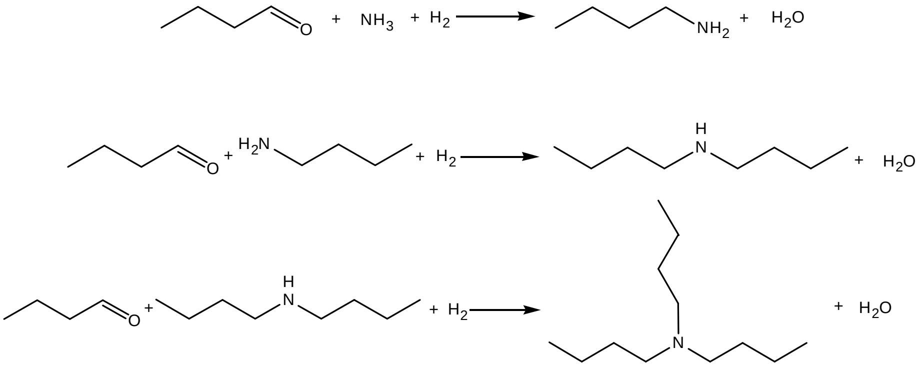
The reactions were conducted mostly at 50 bar and at 50 and 80 ºC. The products were analyzed by using a Hewlett Packard 5890A gas chromatograph equipped with a DB Wax 1701 column and FID detector. Pure butylamine dibutylamine and tributylamine were used for the identification of the main products in the reaction mixtures. GC/MS analyses were performed in order to identify reaction intermediates. The metal leaching was followed by XRF analysis of the filtered reaction mixtures. Rhodium was found not to dissolve during one catalytic cycle at a detection limit of 0.002%.

Experiments were done in order to find whether mass transfer rate limitations occurred or not for the highly active catalysts. According to results obtained, mass transfer limitations of hydrogen diffusion from liquid to solid did not influence the measured reaction rates.

RESULTS AND DISCUSSION

Graphite and charcoal were chosen as catalyst support as it was expected that these materials will have little effect on the reacting carbonyl compound or intermediates in contrast to oxide supports (basic or acidic) that could induce unwanted and very different transformations of the substrate.

In the product mixture resulted during the reductive amination of butanal with ammonia and hydrogen over supported noble metal catalysts butylamine, dibutylamine and tributylamine were identified. According to the obtained analysis results, the reactions occurring in the reactor under the working conditions used (V_{EtOH} = 8 cm^3, $n_{Butanal}$ = 0.0222 mol (2 cm^3), n_{NH3} = 0.3235 mol, $n_{NH3}/n_{Butanal}$ = 14.57, $V_{EtOH}/V_{Butanal}$ = 4, p = 50 bar, T = 323-353 K) are given in Scheme 1.



Scheme 1. Main chemical reactions during the reductive amination of Butanal.

The hydrogen consumption (normalized to moles of metal in the catalysts) indicates that Pt and Rh are the most active metals (Fig.1).

The very high activity of 5%Rh/charcoal relative to 5%Rh/HSA graphite (HSA = high surface area) can be attributed to the high surface area of the charcoal support, which resulted in a higher metal dispersion. The increased activity of 5%Pt/HSA graphite versus 5%Pt/LSA graphite can be attributed to the higher metal dispersion of the 5%Pt/HSA graphite catalyst.

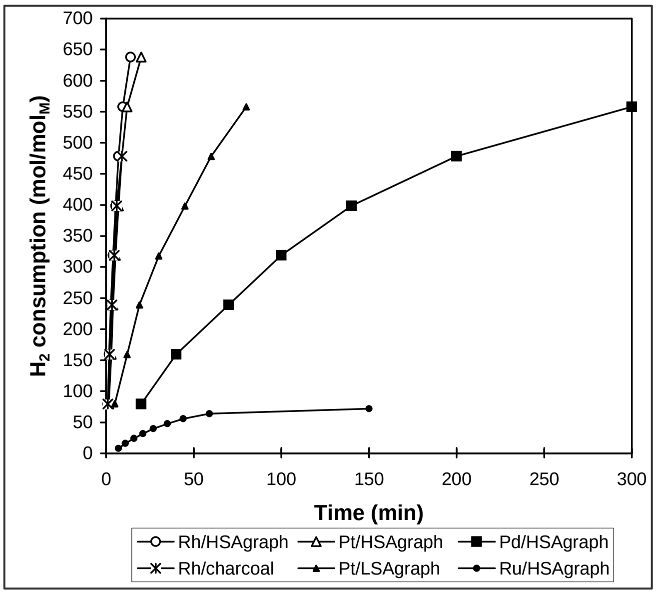


Fig. 1. Hydrogen consumption normalized to moles of metal as a function of reaction time for the reductive amination of butanal over carbon supported noble metal catalysts (n_M: moles of metal, $n_M = 2.22\cdot10^{-5}$ mol, $n_{Ru} = 2.22\cdot10^{-4}$ mol, $n_{Butanal} = 0.0222$ mol, $n_{NH3} = 0.3235$ mol, $n_{NH3}/n_{Butanal} = 14.57$, p = 50 bar, T = 353 K).

Fig. 2 illustrates the final yields of the corresponding amines over the catalysts tested.

The less active 5%Ru/HSA graphite showed the highest selectivity towards butylamine followed by 5%Rh/charcoal and 5%Rh/HSA graphite. 5%Pt/LSA graphite (LSA = low surface area) and 5%Pt/HSA graphite directed the reductive amination of butanal mostly to dibutylamine. 5%Pd/HAS graphite and 5% Pd/charcoal were the least selective catalysts, yielding primary, secondary, and tertiary amines at almost the same level (see Fig 2). As for platinum and palladium catalysts, the selectivity observed for the two Rh based catalysts was also almost the same, allowing us to conclude that the selectivity during reductive amination of butanal is mostly metal dependent, and is little influenced by the support.

Fig. 3 indicates the rates of formation (TOFs, global rates normalized to moles of metal) of butylamine, dibutylamine, and tributylamine over the tested catalysts. The rate over 5%Rh/charcoal was ~3-4 times higher than over 5%Rh/HSA graphite and 5%Pt/HSA graphite, ~5-6 times higher than over 5%Pt/LSA graphite and Pd/charcoal, ~40 times higher than over 5%Pd/HSA graphite, and about 75 times higher than over 5%Ru/HSA graphite. The highly selective ruthenium based catalyst had the lowest activity. As observed in case of hydrogen consumption with reaction time, the rates of the product formation were also strongly correlated to the BET area and the metal dispersion of the catalysts.

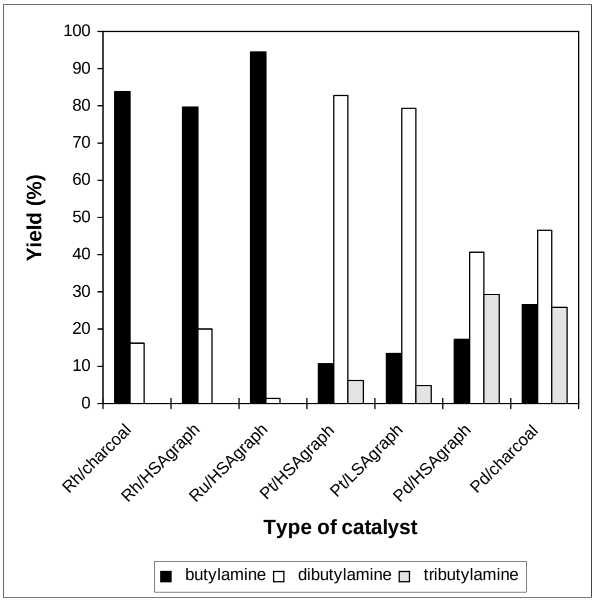


Fig. 2. Final yields of the corresponding amines for the reductive amination of butanal over carbon supported noble metal catalysts (n_M: moles of metal, $n_M = 2.22\cdot10^{-5}$ mol, $n_{Ru} = 2.22\cdot10^{-4}$ mol, $V_{EtOH} = 8$ cm^3, $n_{Butanal} = 0.0222$ mol, $n_{NH3} = 0.3235$ mol, $n_{NH3}/n_{Butanal} = 14.57$, p = 50 bar, T = 353 K).

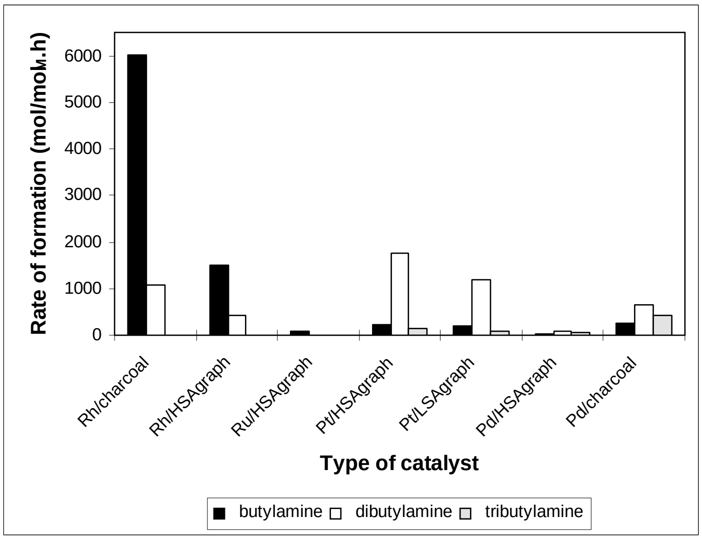


Fig. 3. Rates of formation of the butylamine, dibutylamine and tributylamine during reductive amination of butanal on carbon supported noble metal catalysts (n_M: moles of metal, $n_M = 2.22\cdot10^{-5}$ mol, $n_{Ru} = 2.22\cdot10^{-4}$ mol, $n_{Butanal} = 0.0222$ mol, $n_{NH3} = 0.3235$ mol, $n_{NH3}/n_{Butanal} = 14.57$, p = 50 bar, T = 353 K).

The reductive amination of butanal strongly depends upon the noble metal used in the catalyst (see Figs. 1-3). Among the catalysts investigated, Rh and Pt based showed the highest activity. The Ru based catalyst had the lowest activity, but the highest selectivity for butylamine. Tributylamine was detected only during reductive amination of butanal over supported Pt and Pd catalysts underlining that selectivity is metal dependent.

Charcoal appears to be a good support providing high activity and selectivity for the supported Rh catalyst and leads to significantly more active catalysts than graphite (see Figs. 1 and 3). In case of Pd, the charcoal supported catalyst was also more active than the graphite supported one (see Fig. 3). This shows that the nature of the carbon support influences the catalytic properties. It is noteworthy that the metal dispersion of the charcoal supported Pd catalyst is almost twice as high (see Table 1) than of Pd/HSA graphite. The reaction rate measured for the same type of metal seems to strongly depend on the metal dispersion of the catalysts (see Table 1 and Fig. 3 for Rh, Pd and Pt catalysts). In contrast, the selectivities for the two rhodium (two palladium or two platinum) catalysts on charcoal and graphite, respectively, are very close (see Fig. 2). The support, thus, influences only the activity and not the selectivity, having an important role in the stabilization of the metal dispersion.

More detailed studies were focused on 5%Rh/HSA graphite catalyst. Fig. 4 shows the yields for the reductive amination of butanal at 353 K and 50 bar total pressure (~ 28 bar hydrogen pressure) over 5%Rh/HSA graphite catalyst as a function of reaction time.

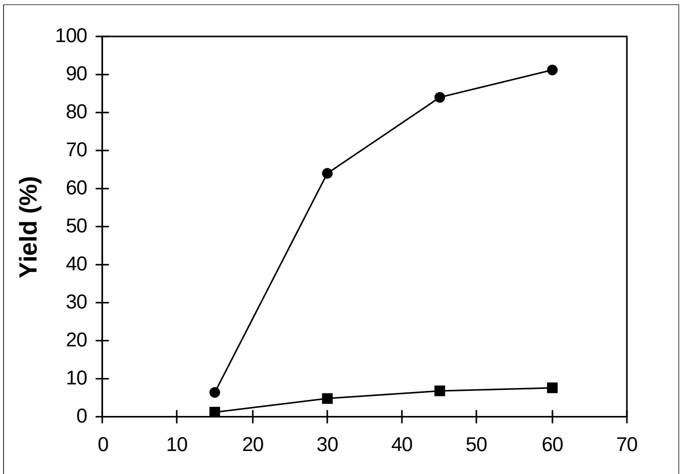


Fig. 4. Yields of butyl- and dibutylamine versus reaction time on 5%Rh/HSA graphite catalyst ($n_{Rh} = 1.11 \cdot 10^{-5}$ mol, $n_{Butanal} = 0.0222$ mol, $n_{NH3} = 0.3235$ mol, $n_{NH3}/n_{Butanal} = 14.57$, p = 50 bar, T = 353 K).

Concerning the products, the reaction seems to have an induction period (see Fig.4), which is not reflected in the hydrogen consumption (being quite fast at the beginning of the reaction). The yield of dibutylamine followed a slow (almost linear) increase with time, while the yield of butylamine after a fast increase became almost parallel with the yield of secondary amine.

When the experiment was repeated at 323 K and 50 bar (~ 37 bar hydrogen pressure), the apparent induction period was longer and the selectivity to primary and secondary amine was different. The yields for the butylamine were lower, and for the dibutylamine higher, compared to those obtained at 353 K. For comparison, Fig. 5 illustrates the dependence of the selectivity in butylamine versus reaction time obtained on 5%Rh/HSA graphite at 323 K and 353 K.

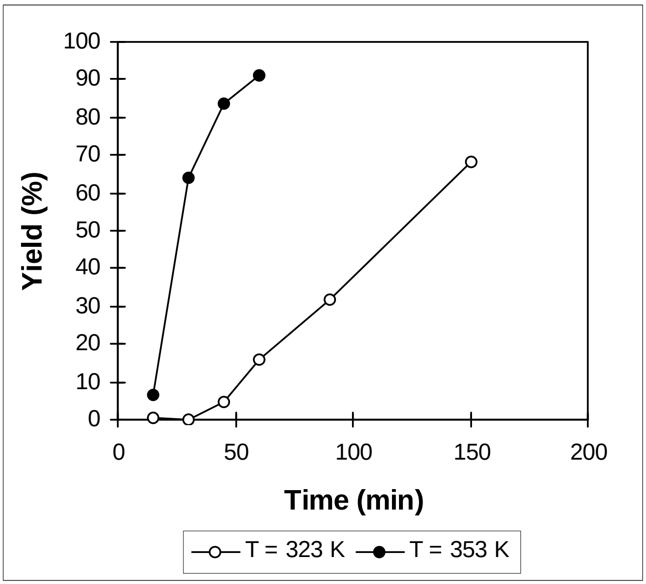


Fig. 5. Selectivity towards butylamine versus reaction time at 323 K and 353 K during the reductive amination of butanal over 5%Rh/HSA graphite catalyst ($n_{Rh} = 1.11 \cdot 10^{-5}$ mol, $n_{Butanal} = 0.0222$ mol, $n_{NH3} = 0.3235$ mol, $n_{NH3}/n_{Butanal} = 14.57$, p = 50 bar).

The evolution of the amines during the reaction over 5%Rh/HSA graphite catalyst (Fig. 4) indicates that butylamine and dibutylamine apparently are primary products. The secondary amine is formed in parallel with the primary amine and the primary amine is not consumed at higher conversions or reaction times. This suggests that butylamine and dibutylamine are formed from the same intermediate.

From the data obtained in this study it is striking to note that metals that are good hydrogenolysis catalysts, such as Rh and Ru [17,18], are selective for producing butylamine, while catalysts that are good hydrogenation catalysts, such as Pt and Pd [17,18], catalyze the preferential formation of dibutyl- and tributylamine.

CONCLUSIONS

Among the studied carbon supported catalysts the Rh and Pt based ones show the highest activity in the reductive amination of butanal. The Ru based catalysts had the lowest activity, but the highest selectivity for the primary amine. Tertiary amine was detected only in the product mixtures obtained over Pt and Pd catalysts. This observation underlines the major role of metal in determining the activity and selectivity of the supported catalysts.

Charcoal appears to be a good catalyst support providing high activity and selectivity for the supported Rh catalyst being significantly more active compared to Rh/graphite. This emphasizes the important role of the support materials. The support seems to influence the activity, but not the selectivity of the catalyst. The BET area and especially the metal dispersion have a strong influence on the catalyst activity for the reductive amination of butanal

Rhodium was found not to dissolve from 5% Rh/charcoal and 5%Rh/HSA graphite catalysts during one catalytic cycle.

Good hydrogenolysis catalysts such Ru and Rh tend to produce mostly primary amine, while metals that have high hydrogenation capacity (Pt and Pd) tend to yield mostly secondary and tertiary amines.

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