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The chemoselective hydrogenation of tallow nitriles to unsaturated 1° fatty amines with carbon modified Ni catalysts

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Abstract

Primary unsaturated fatty amines are typically produced by the hydrogenation of unsaturated fatty nitriles in a batch process with activated Ni catalysts, where the required level of carbon–carbon double bond retention is determined by the fatty amine's use. At low to moderate levels of nitrile conversion the metal's surface is completely covered with the adsorbed nitrile and practically no olefin adsorption takes place. At high levels of nitrile conversion the surface is not saturated and this allows the olefinic groups to adsorb and hydrogenate as the batch process comes to an end. We have drastically improved olefin retention at low nitrile coverages by controlling the active site's ensemble size via the deposition of carbonaceous residues onto the catalyst's surface. This stifled the co-adsorption of the weakly held olefinic groups during nitrile hydrogenation and enhanced their steric hindrance caused by their internal position along the fatty chain to give higher unsaturated primary fatty amine yields. These carbonaceous residues were formed by the decomposition of formaldehyde or sodium formate onto the catalyst's surface at different temperatures. Although these treatments slightly decreased the initial activity, all of them increased olefin retention [as calculated from iodine value (IV) titrations], decreased the titrated level of secondary and tertiary amines (2/3 A) and led to higher nitrile conversions [as determined by total amine value (TAV) titrations] within shorter reaction times. The formaldehyde treatment was preferred and gave the highest olefin retention (∼98%) at a very high nitrile conversion (∼95%). This work will also describe the effects of catalyst particle size and ammonia pressure on tallow nitrile hydrogenation.

Keywords: Unsaturated fatty nitriles; Hydrogenation; Ni catalysts; Carbonaceous residue; Primary unsaturated fatty amines

1. Introduction

Primary fatty amines are used for the production of cationic surfactants (textile softeners, dyeing aids, anti-static agents, germicides, bactericides and pigment aids), amphoteric surfactants (detergents and shampoos), corrosion inhibitors, asphalt emulsifiers, releasing agents for molded rubber parts, anti-caking agents for fertilizers, fuel additives and sludge inhibitors. Fig. 1 shows how plant and animal triglycerides are converted into commercially useful products and this paper will focus on the selective hydrogenation of unsaturated fatty nitriles to unsaturated fatty amines with high levels of olefin retention. The fat source for these nitriles is beef tallow with a mixture of carbon chain lengths ranging from 14 to 20, where the vast majority has 18 with a sizable contribution from those with 16 [1]. The unsaturation level of tallow nitrile mixtures is typically measure by the iodine titration of olefin groups and this is commonly referred to the mixture's iodine value (IV). Typically tallow nitriles have IV ranging from 30 to 60 and they are predominately made up of C18:0 (C18:0 indicates that it has 18 carbon atoms and 0 double bonds), C18:1, C18:2 and C16:0 with some C18:3 and C16:1 accompanied with traces of the other fatty nitriles. One of the many examples of this reaction is displayed in Fig. 2 for the stepwise conversion of a C18:3 fatty nitrile to a C18:3 fatty amine that can be eventually hydrogenated to a C18:0 fatty amine. As Fig. 2 indicates, the nitrile group is initially hydrogenated and as its surface coverage decreases at higher nitrile conversions, the olefinic groups will randomly start to hydrogenate to form a mixture of C18:2, C18:1 and C18:0 fatty amines until complete saturation is reached. Liquid fatty amines have high levels of unsaturation where practically all of the olefins have retained their *cis* configuration with very little (if any) formation of secondary (2°) or tertiary (3°) amines. Since many of the high value

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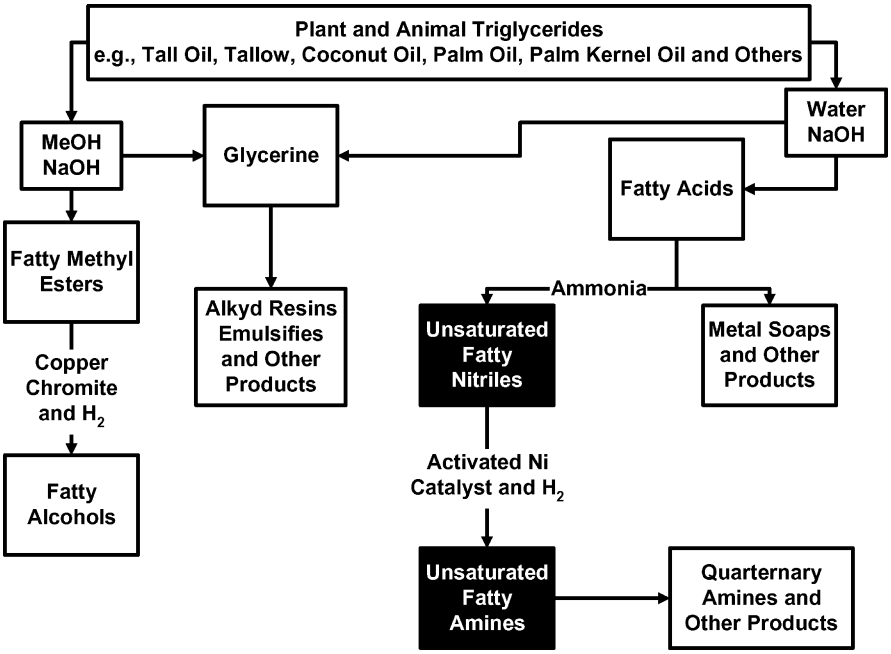

Fig. 1. The conversion of plant and animal triglycerides into commercially useful products.

products require liquid fatty amines, it is important to have a catalyst that selectively hydrogenates the nitrile group to completion with a high level of *cis* olefin retention while avoiding the formation of 2° and 3° amines. This work will describe the preparation of such a catalyst and the theoretical basis behind its development.

2. Experimental

The two untreated activated nickel catalysts used in this study have average particle sizes (APS) of ~28 and ~53 μm and both of them are commercially available from Degussa AG in Hanau, Germany. These catalysts were generated via the

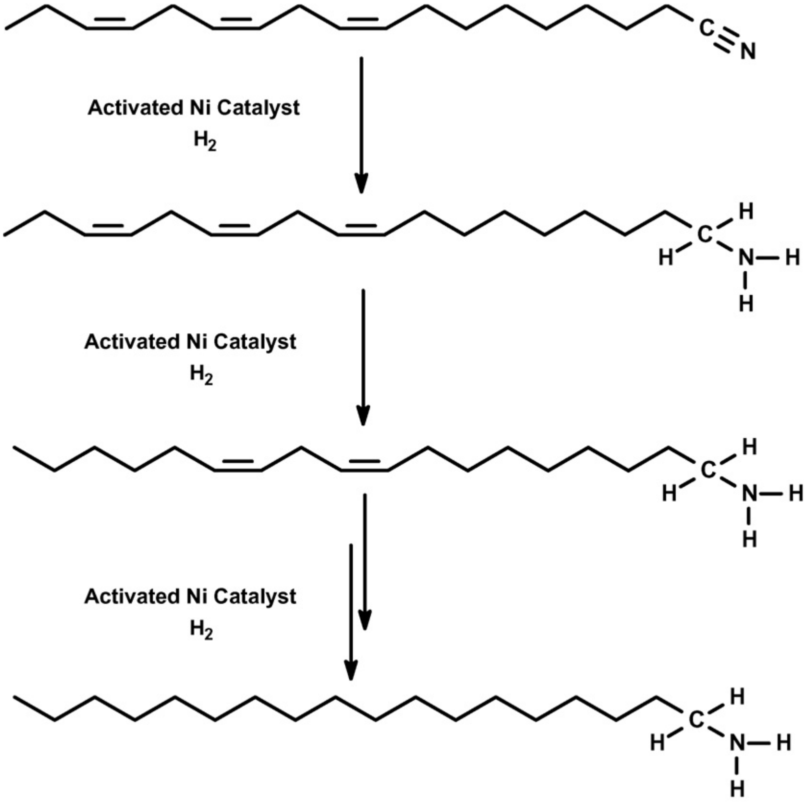

Fig. 2. The stepwise conversion of a C18:3 fatty nitrile to a C18:2 fatty amine and eventually a C18:0 fatty amine.

caustic leaching of most of the aluminum from a 53% Ni/47% Al alloy resulting in hydrogen rich catalysts having highly dispersed aluminum stabilized nickel crystals (~10 nm) [2]. These catalysts were also treated with either an aqueous suspension of formaldehyde at room temperature or sodium formate at either room temperature or 90 °C. These treatments were performed with 1.3 mmol modifier/g catalyst. Additional information about these treatment procedures can be found under Ostgard et al. [3].

The characterization of the catalysts with and without formaldehyde treatment was performed by the use of temperature-programmed oxidation (TPO). To perform TPO, about 5–10 g of the water-moist catalyst was dried in a stream of nitrogen flowing 10 l/h at 120 °C for a period of 17 h. The furnace was then carefully cooled to 20 °C. After reaching a constant reactor temperature, the pure nitrogen was switched to 4% oxygen in nitrogen passing over the catalyst at the rate of 10 l/h while the temperature was ramped at the rate of 6 °C/min to the end temperature of about 800 °C. The oxygen content was measured during the experiment with an "Oxynos 100" paramagnetic detector and the amount of consumption was determined from the area of the oxygen curve. The CO_2 and CO contents were determined by their specific detectors. In these experiments only CO_2 was detected.

The low-pressure hydrogenation of nitrobenzene was carried out over 1.5 g of these catalysts in 110 ml of an ethanoic 9.1 wt.% nitrobenzene solution at 25 °C and atmospheric pressure. These hydrogenations were performed in a baffled glass reactor outfitted with a sparging stirrer spinning at 2000 rpm [4].

The slurry phase hydrogenation of a tallow nitrile mixture consisting predominantly of C18 and C16 with a small amount of C14, C20 and other long chain aliphatic fatty nitriles with a iodine value (IV) of ~51 was carried out in a 1 l steel autoclave. Initially the autoclave was charged with 1 g of catalyst (on a dry basis) and 500 g of the above-mentioned tallow nitrile followed by three purges with nitrogen and then three purges with ammonia. The reagent was then saturated with 6 bar of ammonia while stirring the mixture at 2000 rpm followed by ramping from room temperature to 140 °C in about 90 min. After reaching 140 °C, the stirring was stopped, the ammonia pressure was adjusted to the desired value (10, 17 or 20 bar), hydrogen was added to bring the pressure to 40 bar and the reaction was started by stirring at 2000 rpm. Samples were taken from the reaction mixture during the hydrogenation for the determination of their iodine value (IV), secondary and tertiary amine value (2/3 A) and the total amine value (TAV). These measurements were also made for the fresh tallow amine for comparison to the reaction mixtures. The IV was determined by a modified Wijs method similar to method Tg 1-64 of the American Oil Chemists' Society (AOCS) where the only difference was the use of cyclohexane instead of carbon tetrachloride. In principle, the determination of the IV is done by the iodine titration of the olefinic bonds in the unsaturated fatty amine and high IV are an indication of higher levels of unsaturation. The 2/3 A value was determined by the official AOCS method Tf 2a-64 and the TAV was measured via the AOCS potentiometric titration method Tf 1a-64. The TAV is the mg of KOH equivalent to the basicity in 1 g of the fatty amine and as this value increases, so does the conversion of the fatty nitrile to the fatty amine. However, the formation of 2° and 3° amines will also decrease this value and one needs to keep this in mind. The 2/3 A value is the mg of KOH equivalent of 2° and 3° amine basicity in 1 g of the fatty amine and higher values are an indication of a lower selectivity in the formation of the desired 1° fatty amine.

3. Results and discussion

3.1. Characterization of the formaldehyde treated activated Ni catalysts

The TPO analyses of many different catalyst types [5] have provided us the basis for the interpretation of TPO profiles measured here. The sharp oxygen uptake peak between 90 and 160 °C is due to the oxidation of the catalyst's hydrogen and it correlates well to its hydrogen content. The broad oxygen uptake peak between 160 and 300 °C is due to the oxidation of surface Ni along and some of the most readily accessible subsurface Ni. The bulk oxidation of the less accessible Ni begins at 300 °C and it is rarely complete during the timeframe of these experiments. Fig. 3 displays the TPO characterization of an untreated activated Ni catalyst and it shows the typical ratio of hydrogen content to accessible Ni (both surface and slightly subsurface) for the type of catalyst used here. Fig. 4 shows the TPO profile for the formaldehyde treated catalyst, where there appears to be a slight enhancement of oxygen uptake from 200 to ~380 °C that is mirrored by the desorption of CO_2 (CO was not formed during this experiment). The formation of CO_2 is from the oxidation of carbonaceous deposits that were generated by the formaldehyde treatment. By comparing Fig. 4 to Fig. 3, it is clear that the formaldehyde treated catalyst still contains a considerable amount of hydrogen and the structure of the catalyst is mostly intact. In other words, the major differentiating factor between the formaldehyde treated and the untreated catalysts is the deposition of carbonaceous residues due to formaldehyde decomposition and there does not seem to be any catalyst restructuring during this process. Table 1 displays the O_2 uptake of these catalysts during TPO and the nitrobenzene activity of

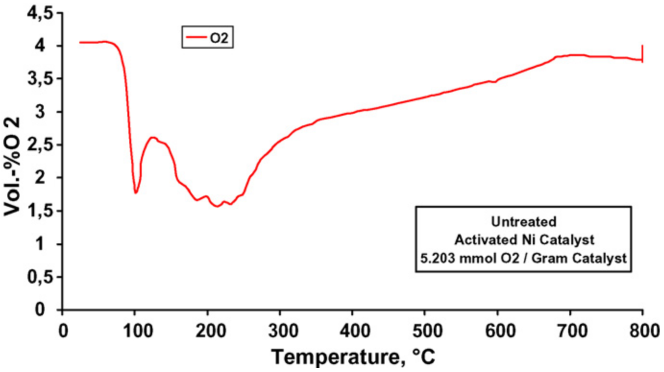

Fig. 3. The TPO characterization of the untreated activated Ni catalyst.

Table 1
The comparison of the formaldehyde treated catalyst to the untreated one

Treatment	TPO O_2 uptake (mmol O_2/g catalyst)	Nitrobenzene hydrogenation activity (ml H_2/min g catalyst)
None	5.203	28
Formaldehyde	4.592	9

these catalysts. Even though the formaldehyde treated catalyst-generated oxygen consuming CO_2 during its TPO, its overall TPO oxygen uptake was lower than the fresh one. This is an indicating that the catalyst was also slightly oxidized during this treatment and that is what one would expect from the decomposition of formaldehyde on the surface.

It was found by Richter and Ho that formaldehyde disproportionates over Ni (1 1 0) surfaces at low temperature (95 K) to form methanol and carbon monoxide [6]. Studies on the chemisorption of CO over Ni have shown that both the bridged and linear species are formed and their amounts are dependent on the surface coverage and temperature, where desorption starts around 170 °C [7–10]. This is in accordance with our TPO data (Fig. 4), where the adsorbed residue was stable up to 200 °C under TPO conditions before it formed CO_2. We had also found methanol in the solution phase at the beginning of this treatment before it was readsorbed and converted into an adsorbed residue [11]. It is also possible that the adsorbed CO could be reduced to formaldehyde during the hydrogenation of tallow nitriles, however, Newton and Dodge [12] found that Ni at even at 200 °C is far more likely to decompose formaldehyde to CO and H_2 ($K_{\text{decomposition}} = 1800$) than it is to hydrogenate CO to H_2CO ($K_{\text{hydrogenation}} = 2.3 \times 10^{-5}$). Hence, it is assumed that any adsorbed CO created during the decomposition of formaldehyde (and possibly methanol) remains stable during the conditions used here for the hydrogenation of tallow nitriles (140 °C and up to 30 bar of hydrogen). Blocking the surface in this way would decrease the number of contiguous atoms available for the formation of an active site (i.e. the ensemble size). Since nitrobenzene adsorbs on the Ni surface by both its phenyl and nitro groups, a drop in its hydrogenation rate would indicate that the ensemble size of the catalyst's active sites has decreased. Table 1 shows that the nitrobenzene activity of the formaldehyde treated catalyst is ~68% lower than the fresh one, thus confirming that this treatment provides a method for ensemble control. Hence formaldehyde decomposes onto the catalyst's surface to form strongly adsorbed CO and other residues on the metal that function as site blockers and potentially as electronic modifiers of the nearby active sites while maintaining the overall structure and most of the hydrogen content of the catalyst.

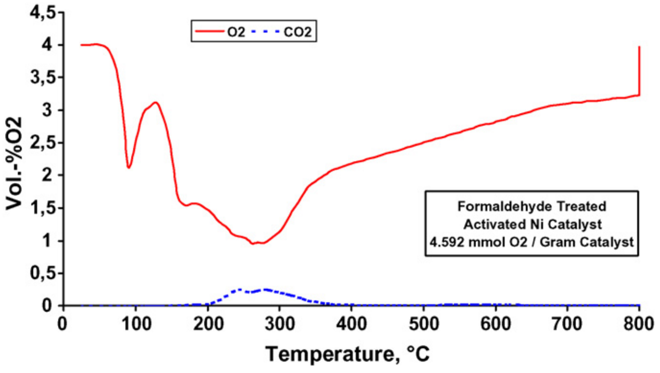

Fig. 4. The TPO characterization of the formaldehyde treated activated Ni catalyst.

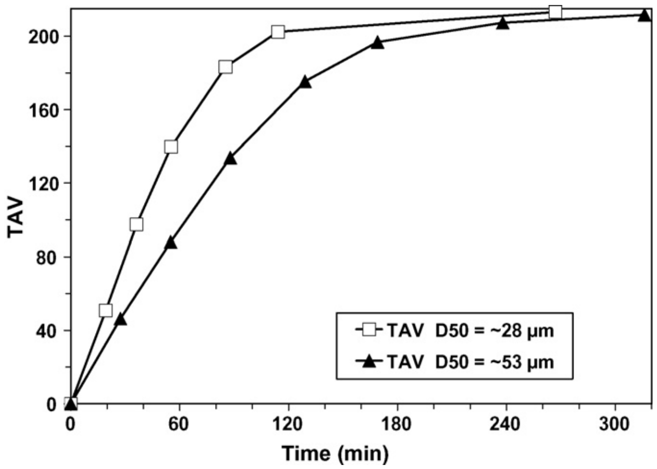

Fig. 5. The effect of catalyst particle size on the TAV during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

3.2. The hydrogenation of tallow nitrile—the effect of catalyst particle size

One of the most important properties of an activated Ni catalyst is its particle size due to its influence on the activity, settling behavior and filterability of the catalyst. Fig. 5 shows the effect of catalyst particle size on the TAV during the hydrogenation of tallow amine. The TAV is an indication of conversion (TAV of ~216 corresponds to 100%) and the increase of the TAV with respect to time is somewhat slower for the catalyst having an APS of ~53 μm in comparison to the one with ~28 μm. This can also be seen in Table 2 where the initial hydrogenation rate of the catalyst with the larger APS is 40% slower than the finer one. However, the time it takes to reach the end of hydrogen uptake is only 25% longer for the coarser catalyst. It would seem that the APS is slightly less important for the overall reaction time than it is for the initial reaction rate. Clearly the catalyst with the smaller APS has the highest amount of accessible external catalytic surface area (outside of the pore system) and this plays an important role in the activity of the catalyst. Fig. 6 displays the effect of the APS on the 2/3 amine value. Even though the finer catalyst forms the 2° and 3° amines faster, the end 2/3 amine values for both of these catalysts seem to be roughly the same. Hence, the APS does not influence final amount of 2° and 3° amines generated at these reaction conditions. The same trend can be seen for the %IV retention as seen in Fig. 7, where the final amount of olefin hydrogenation is not affected by the APS. Since the %IV retention is dependent on the catalyst's level of nitrile surface coverage that keeps the olefins from adsorbing and hydrogenating, it is best to plot the

Table 2
The reaction summary for the hydrogenation of tallow nitriles

APS[a] (μm)	Treatment	NH_3 pressure (bar)	Initial activity[b]	Reaction time[c] (min)	%IV retention	2/3 amines	TAV
53	None	10	1.52	277	51	9.7	212
28	None	10	2.55	222	46	9.3	213
28	None	17	1.63	300	45	6.5	213
28	None	20	1.28	>300[d]	93	2.4	205
28	H_2CO 25 °C	10	1.57	221	84	6.7	216
28	H_2CO 25 °C	17	1.20	256	92	4	216
28	HCO_2Na 25 °C	10	2.85	230	52	8	211
28	HCO_2Na 90 °C	10	1.78	258	54	9.5	211

[a] APS = average particle size.
[b] mol/min g catalyst.
[c] The reaction time determined by hydrogen uptake measurements.
[d] The reaction at 20 bar did not come to completion within 300 min.

%IV retention against the TAV as seen in Fig. 8. The %IV retention is close to 100% at low nitrile conversions and high nitrile coverages. However, as the concentration of the nitrile decreases, more of the olefins are adsorbed and reduced as seen by the rapid drop in the %IV retention after the TAV of 200 has been reached. Since both the finer and coarser catalysts have the same %IV retention versus TAV plots, it could be concluded that the APS does not control the percentage of olefin retention under these reaction conditions.

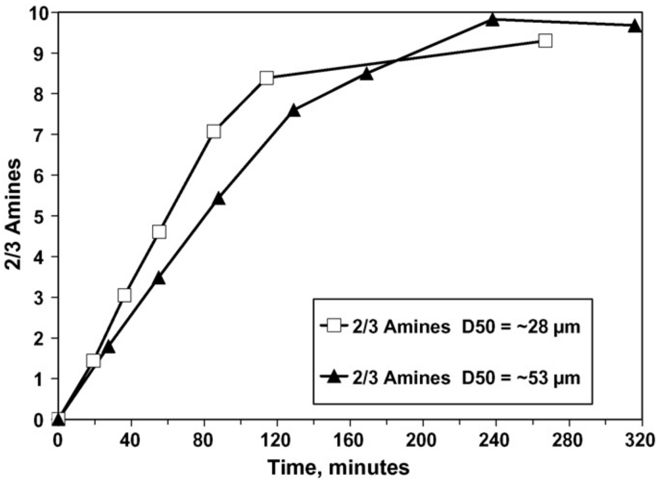

Fig. 6. The effect of catalyst particle size on the 2/3 amine value during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

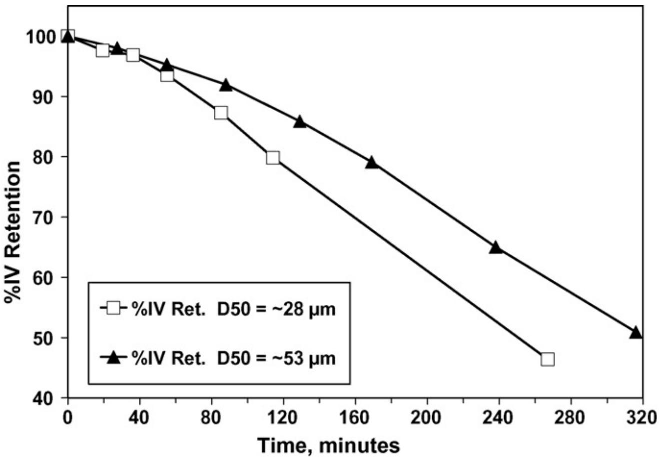

Fig. 7. The effect of catalyst particle size on the %IV retention during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

3.3. The hydrogenation of tallow nitrile—the effect of ammonia pressure

The amount of ammonia present during the hydrogenation of tallow amines is decisive for the avoidance of 2° and 3° amines, the retention of olefins, the initial reaction rate and the time it takes to bring the reaction to completion. As the ammonia pressure increases, it starts to adsorb on the catalyst's surface more competitively. This leads to a lower initial reaction rate, a longer reaction time, higher levels of olefin retention and lower levels of 2° and 3° amines as displayed in Figs. 9–11. The overall effect of ammonia pressure on the hydrogenation of tallow amines is not linear. The relative scale of improvements in olefin retention and 1° amine formation were much greater when the ammonia pressure was increased from 17 to 20 bar than when it was increased from 10 to 17 bar. The use of higher ammonia pressures is especially useful for the avoidance of 2° amines since they are formed via an

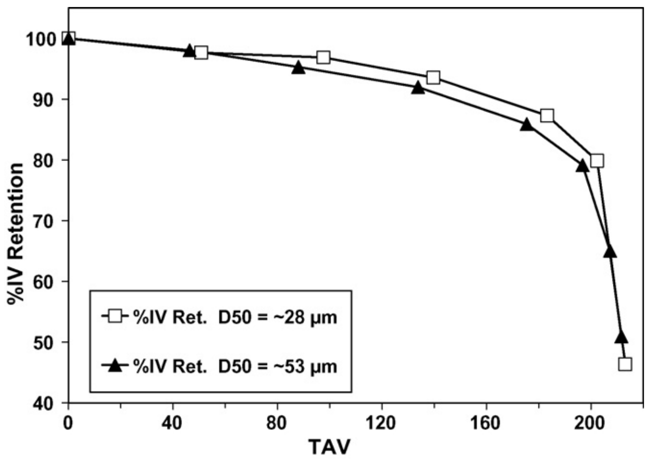

Fig. 8. The effect of catalyst particle size on the %IV retention during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3) as monitored by the TAV.

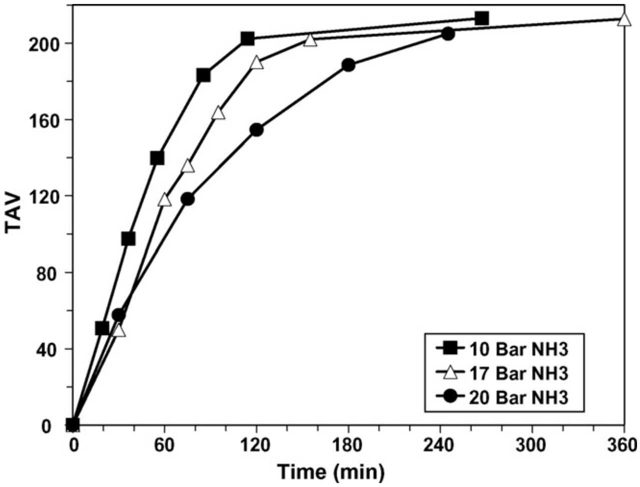

Fig. 9. The effect of ammonia pressure on the TAV during the hydrogenation of tallow amines (140 °C, 30–20 bar H_2 and 20–10 bar NH_3).

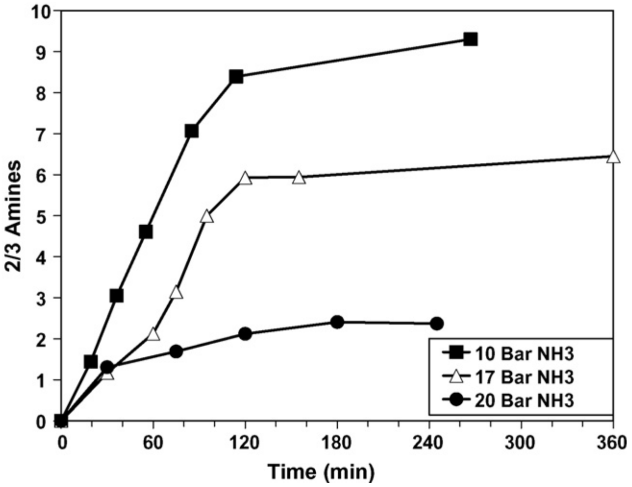

Fig. 10. The effect of ammonia pressure on the 2/3 amine value during the hydrogenation of tallow amines (140 °C, 30–20 bar H_2 and 20–10 bar NH_3).

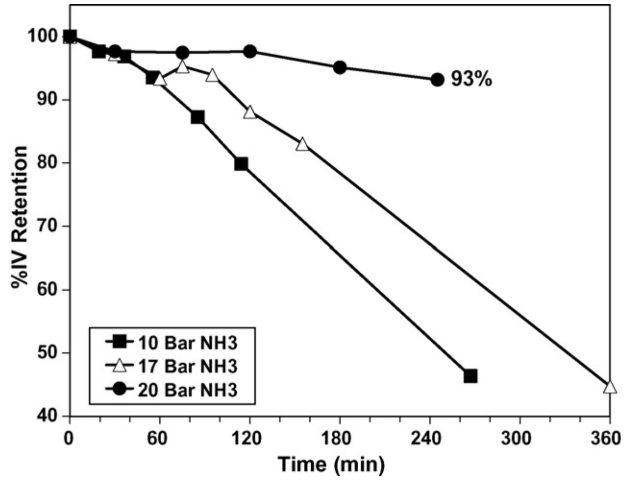

Fig. 11. The effect of ammonia pressure on the %IV retention during the hydrogenation of tallow amines (140 °C, 30–20 bar H_2 and 20–10 bar NH_3).

equilibrium step that generates ammonia and the presence of more ammonia will push this equilibrium towards the 1° amine. In this way, the yield of the 1° amines is improved in a non-linear stepwise fashion as the pressure is increased from 10 to 17 and eventually to 20 bar. This is not the case for olefin retention as seen in Fig. 12. There is not an improvement in olefin retention when the ammonia pressure is increased from 10 to 17 bar. However, there is a very strong enhancement of olefin retention as the ammonia pressure goes from 17 to 20 bar. The data suggests that the olefinic groups of tallow amines and nitriles can competitively adsorb and hydrogenate at low levels of nitrile surface coverage (i.e. high nitrile conversion) when the ammonia pressure is 17 bar or lower. When the ammonia pressure is increased to 20 bar, the olefins become less competitive for adsorption sites leading to an extension of the 100% olefin retention trend from a TAV of 97 (for the lower ammonia pressures) to a TAV over 200 to give a final IV retention of 93%.

The decrease in the initial reaction rate is far greater when the ammonia pressure is increased from 10 to 17 bar than it was from the increase from 17 to 20 bar. The increase in the overall reaction time is rather drastic between 10 and 17 bar. However, at 20 bar ammonia, the hydrogen uptake did not even come to completion after 300 min. Hence the levels of ammonia necessary for the most selective reaction may also hurt the completion and the productivity of this process. Needless to say, searching for the right ammonia pressure that gives the desired balance between reaction selectivity and completion is not the best way to run an industrial process and this has led to the development of the treated catalysts used here.

3.4. The hydrogenation of tallow nitrile—the effect of catalyst pretreatment

Because the formaldehyde treated activated Ni catalysts have been found to be more selective for the hydrogenation of fructose to mannitol [13] and pynitrile to the desired grewe

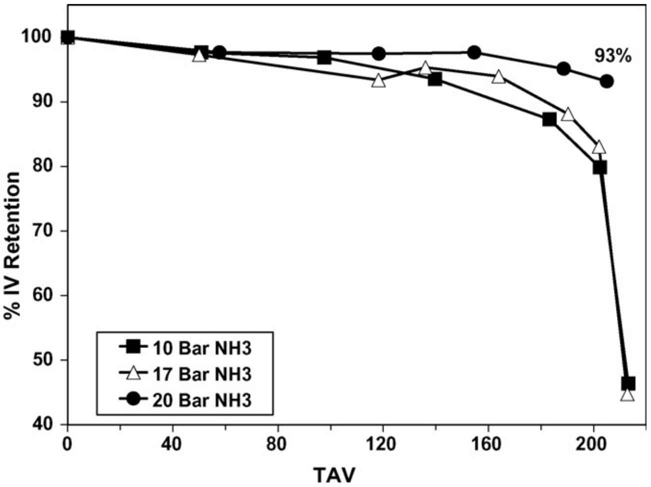

Fig. 12. The effect of ammonia pressure on the %IV retention during the hydrogenation of tallow amines (140 °C, 30–20 bar H_2 and 20–10 bar NH_3) as monitored by the TAV.

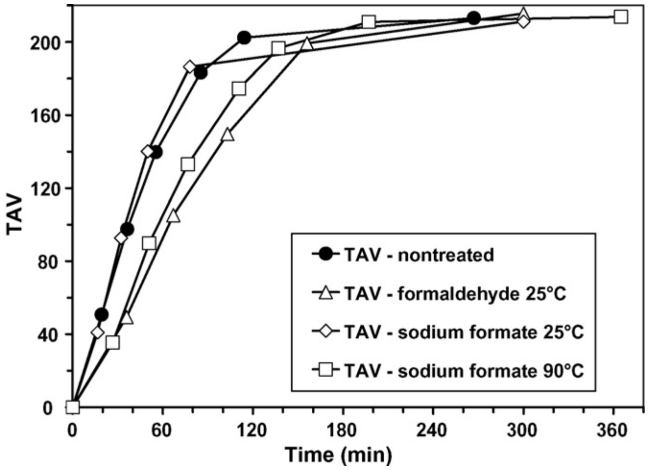

Fig. 13. The effect of catalyst pretreatment on the TAV during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

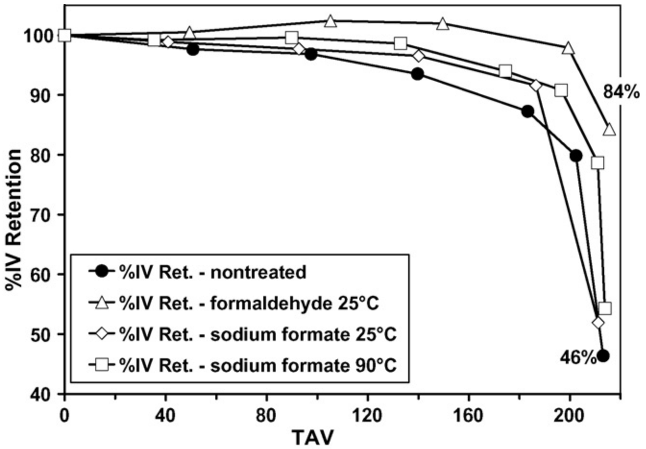

Fig. 16. The effect of catalyst pretreatment on the %IV retention during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3) as monitored by the TAV.

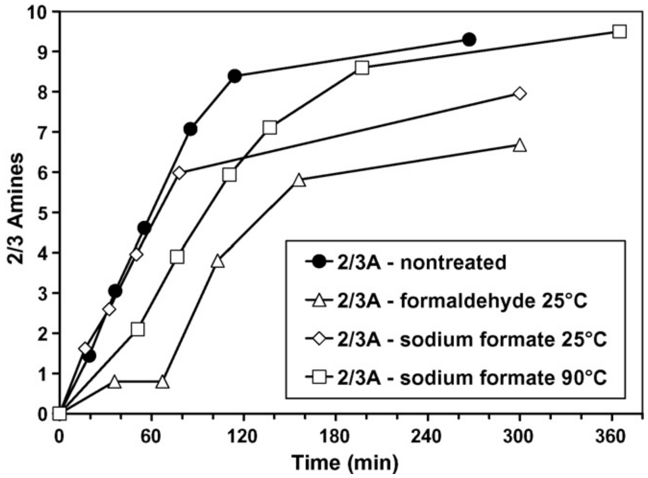

Fig. 14. The effect of catalyst pretreatment on the 2/3 amine value during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

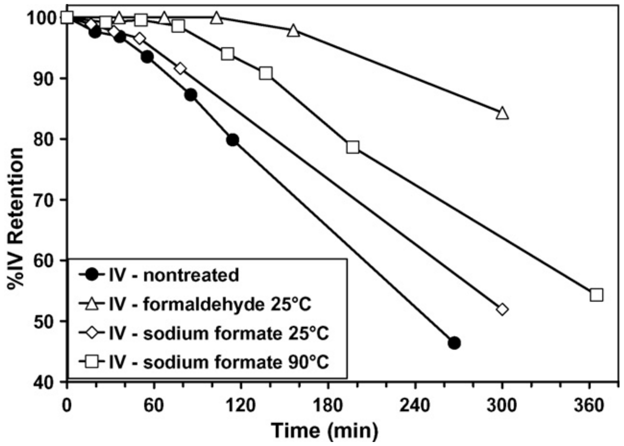

Fig. 15. The effect of catalyst pretreatment on the %IV retention during the hydrogenation of tallow amines (140 °C, 30 bar H_2 and 10 bar NH_3).

diamine for Vitamin B_1 production [14], it was decided to also try them for the chemoselective hydrogenation of unsaturated tallow nitriles to unsaturated tallow amines. Our previous work had also found that sodium formate treated activated Ni catalysts were more selective for the hydrogenation of benzonitrile to benzylamine [3] and these catalysts were also included in this test series. The tallow nitrile hydrogenation results at 10 bar ammonia with these catalysts are displayed in Figs. 13–16, as well as Table 2. The 25 °C sodium formate treated activated Ni catalyst had 11% more initial activity, roughly the same reaction time, a lower 2/3 amine value and a slight advantage in olefin retention over the untreated catalyst. Performing the sodium formate treatment at 90 °C resulted in a 30% decrease in the initial reaction rate, a somewhat longer reaction time, slightly improved olefin retention and roughly the same 2/3 amine value as the untreated catalyst. Increasing the treatment temperature was most noted by the drop in activity and this was probably due to the more effective decomposition of sodium formate on the catalyst's surface. The treatment of the catalyst with formaldehyde at 25 °C provided the most selective surface tested at the ammonia pressures of 17 bar and lower, while maintaining adequate activity at the highest conversion levels see here (TAV = 216). At the ammonia pressure of 10 bar, the formaldehyde treated catalyst generated 28% fewer 2°and 3° amines, had 1.83 times more olefin retention and came to completion at the same time as the untreated catalyst. When this reaction was performed with 17 bar of ammonia (please see Figs. 17–20), the 2/3 amine value was 38% lower, the olefin retention was 2.04 times higher and the over all reaction rate was 15% faster for the formaldehyde treated catalyst in comparison to the untreated one. Even though the formaldehyde treated catalyst had lower initial activities than the untreated ones, this catalyst was able to reach the highest TAV measured here (216) at the same (10 bar) or even faster (17 bar) reaction times. The TAV versus time curves (Figs. 13 and 17) for the formaldehyde treated catalysts were more linear than the untreated ones leading to a more selective hydrogenation that could be more readily controlled.

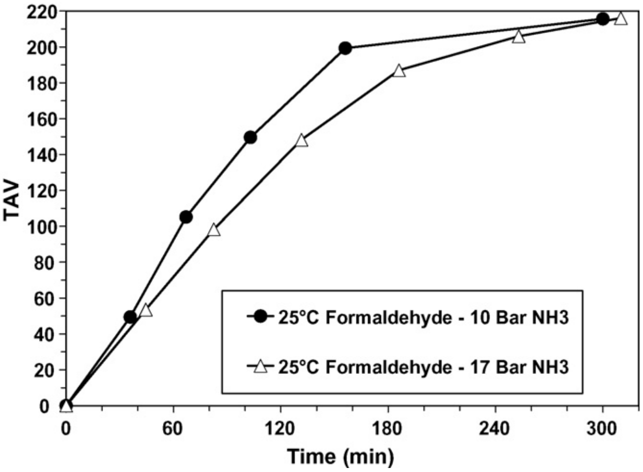

Fig. 17. The effect of ammonia pressure on the TAV during the hydrogenation of tallow amines over formaldehyde treated catalysts (140 °C, 30–23 bar H_2 and 17–10 bar NH_3).

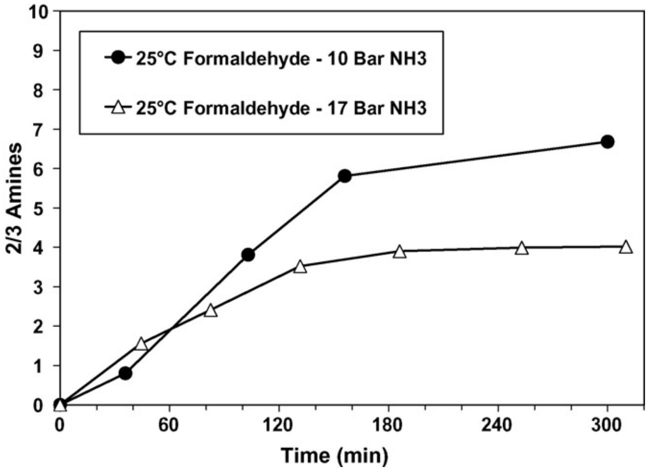

Fig. 18. The effect of ammonia pressure on the 2/3 amine value during the hydrogenation of tallow amines over formaldehyde treated catalysts (140 °C, 30–23 bar H_2 and 17–10 bar NH_3).

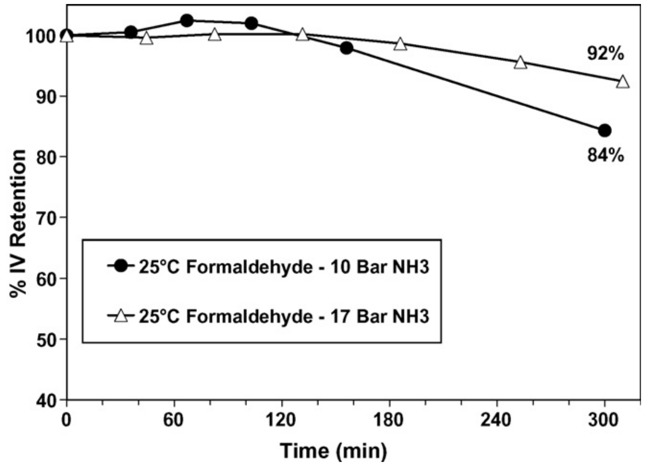

Fig. 19. The effect of ammonia pressure on the %IV retention during the hydrogenation of tallow amines over formaldehyde treated catalysts (140 °C, 30–23 bar H_2 and 17–10 bar NH_3).

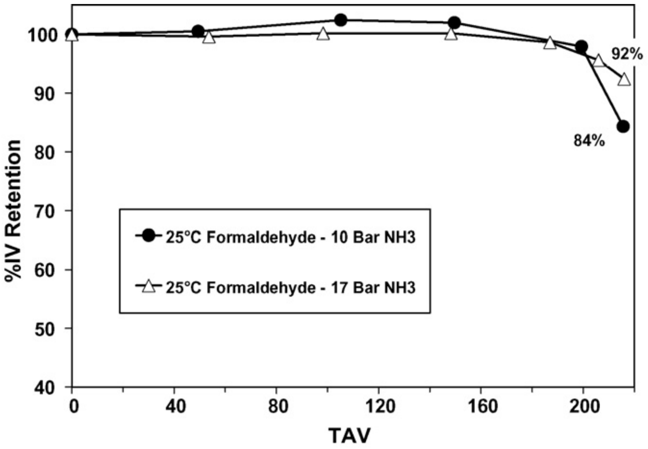

Fig. 20. The effect of ammonia pressure on the %IV retention during the hydrogenation of tallow amines over formaldehyde treated catalysts (140 °C, 30–23 bar H_2 and 17–10 bar NH_3) as monitored by the TAV.

The formaldehyde treated catalyst provided results at 17 bar ammonia that were as selective and active as the untreated catalyst at 20 bar with the added benefit of reaching a TAV of 216 within a reasonable reaction time.

One possible reason for the enhanced performance of the formaldehyde treated catalyst could be due to the optimal ensemble size of its active sites. These ensembles allow for the hydrogenation of the strongly adsorbed nitrile group with very little 2° and 3° amine formation. The 2° amine is formed by the generation and hydrogenation of a ditallow imine that would need to undergo a considerable amount of steric strain before it could adsorb and hydrogenated on the smaller ensembles of the formaldehyde treated catalysts. This would make it more likely for the ditallow imine to react with ammonia to form the alpha amino secondary amine that can be easily split into the tallow amine and tallow imine. Once formed, the tallow imine could be readily hydrogenated on these smaller ensembles to the tallow amine. Hence, the formaldehyde treated catalysts are more effective in using ammonia for selectivity enhancements while maintaining reasonable reaction times. These smaller ensembles also increase the steric hindrance of the olefins located in the middle of the long tallow carbon chains making it more difficult for them to adsorb and hydrogenate. Thus not only do the smaller ensembles improve the use of ammonia as a selectivity enhancer, but they also magnify the natural differentiating factors between the groups of the molecule to provide higher olefin retention, lower 2/3 amine values and higher nitrile conversions at acceptable reaction times.

4. Conclusions

The effect of catalyst particle size on the hydrogenation of unsaturated tallow nitriles to unsaturated tallow amines was limited to the reaction rate as determined by the available amount of external catalytic surface area. There was no correlation between the selectivity of this reaction (e.g. the 2/3 amine value and %IV retention) and the catalysts' particle size. As expected, increasing the ammonia pressure of the reaction does decrease the 2/3 amine value and improve olefin retention at the expense of initial activity, overall reaction time and reaction completion. Finding the right balance between selectivity and reaction completion by the choice of ammonia pressure may not always produce the best results. We have developed a series of activated Ni catalysts with well-defined ensemble sizes that can be controlled by the deposition of measured amounts of modifiers on to the catalytic surface. Although the deposition of sodium formate produced some interesting results, formaldehyde was clearly the modifier of choice. Formaldehyde decomposes onto the activated Ni surface to form strongly held CO and MeOH that can desorb and redeposit back onto the catalyst to generate additional carbonaceous residues. These carbonaceous residues separate the activated Ni surface in to more effective ensembles that readily hydrogenate tallow nitriles with lower 2° and 3° amine formation while maintaining very high levels of olefin retention.

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