Hydrogenation of Citral over Pt and Pt-Sn Catalysts

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Hydrogenation of citral on monometallic (Pt) and bimetallic (Pt-Sn) catalysts was investigated. It was found that the catalyst activities and product distributions were different over Na-Y and Clino supports. Among monometallic catalysts, Pt/Na-Y was more selective to citronellol (3.9%) and unsaturated alcohols, geraniol and nerol, (14.1%). Sn addition increased the catalyst activities. However, its effect on product distribution differed. Yield of geraniol+nerol changed from 5.1% to 19.7% over Clino. However, selectivity to unsaturated alcohols over Na-Y decreased when it was prepared as a bimetallic catalyst support. Unsaturated alcohol formation was favored when there was a metal support interaction over monometallic catalysts, and metal-promoter interaction over bimetallic catalyst.

Key Words: Citral, Pt-Sn, hydrogenation, unsaturated alcohols, citronellal, zeolite catalysts.

Introduction

Citral (α, β unsaturated aldehyde) contains both isolated and conjugated double bonds and a carbonyl group. The hydrogenation reaction of citral is a very complex one and side reactions like acetalyzation and cyclization can occur. In citral hydrogenation, nerol, geraniol, and citronellol are desired products.

Many efforts have been made in recent years for developing a suitable catalytic system able to improve the yields of products of C=O bond hydrogenation. The reaction selectivity has been found to be influenced by several parameters such as particle size, precursors, and the support and presence of promoters. It has been reported that addition of suitable elements (Sn, Ge, Fe, Ge) can strongly modify the catalytic properties of the active metal and so improves the selectivity to unsaturated alcohols.[1,2] Electronic and geometric effects have been suggested as the explanation for the improvement in selectivity towards unsaturated alcohols.

The mode of adsorption of α, β unsaturated aldehyde molecules can be governed by the electronic structure of the metal surface. Thus, enrichment of the metal surface with electrons by interactions with a support or ligand could decrease the binding energy of the C=C bond via an increase of the repulsive 4-electron interaction and, on the other hand, favor the back bonding of interaction with π_{CO}-orbital and the hydrogenation of the C=O bond with respect to that of C=C.[3]

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Supported noble metal catalysts of Pt have been investigated.[4−7] Pt has shown some selectivity to unsaturated alcohols. Addition of tin has been shown to improve their performance and selectivity.[4,8]

Zeolite supports introduce the possibility of metal-support interactions: active metal properties can be polarized by nearby cations or by metal-support interaction.[3] Blackmond et al. reported that selectivity to unsaturated alcohols increased when the support was less acidic.[2] The decrease in acidity results in grater electron density on the metal particles. Alvarez-Rodriguez et al. reported that Ru particles interacted with the support, zeolite KL, when their particle sizes were small (2.8 nm). This induced the maximum citronellal selectivity in the reaction. However, larger Ru particles favored the formation of unsaturated alcohols.[9] High yield of citronellal (90%) was obtained over clinoptilolite rich natural zeolite supported Pd catalyst.[10]

In the present study, the combined effects of support (Na-Y, Clino) and promoter (Sn) on the hydrogenation of citral was investigated. It was aimed to evaluate Na-Y and Clinoptilolite rich natural zeolite as catalyst supports for Pt and Pt-Sn.

Experimental

Preparation of catalysts

The monometallic and bimetallic catalysts were prepared by impregnation and coimpregnation. Na-Y (Zeolyst, CBV100 powder) and clinoptilolite rich natural zeolites (Clino, Manisa–Gördes, Turkey) were used as supports. Clino was the same as the one used by Yılmaz et al., where more details about this material can be found.[10] Clino chunks were crushed and then sieved to a particle size ranging between 38 and 150 μm. These particles were washed with deionized water in a shaking water bath at 80 °C for 2 h. This procedure was repeated twice to remove the water soluble impurities. Washed zeolites were dried overnight at 120 °C. Washed Clino and Na-Y were calcined at 500 °C under N_2 flow of 100 ml/min for 5 h and then used as supports.

The metal precursor salts were platinum(II) acetyl acetonate and $SnCl_2.2H_2O$. The supports were slurried with ethanol solution of precursors for 16 h with magnetic stirrer at room temperature. Afterwards, ethanol was evaporated in a rotary evaporator at 45 °C for 1 h. The impregnated supports were dried in an oven at 120 °C overnight and then calcined at 500 °C under dry air flow (100 ml/min) for 5 h. The Pt loading of the catalysts (0.01 molar Pt solution) was kept constant. Sn/(Sn+Pt) mole ratio was taken as 0.02 for all the catalysts.

Characterization of catalysts

Prepared catalysts were characterized using different instrumental techniques namely scanning electron microscopy (Philips SFEG 30S SEM), elemental analyzer (Varian Liberty II ICP-AES), X-ray diffraction (Philips X'Pert Pro with Cu Kα radiation), and nitrogen adsorption (Micromeritics ASAP 2010).

The acidity of the samples was determined by Temperature-Programmed Desorption of Ammonia (NH_3-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument. The sample was heated up to 500 °C by increasing the temperature at a rate of 5 °C/min and kept at this temperature for 1 h under He gas flow of 70 ml/min. Then the sample was cooled under He flow of 30 ml/min to 90 °C at a rate of 5 °C/min. This was followed by switching the flow to NH_3-He gas mixture at the rate of 30 ml/min for 30 min. Physically adsorbed NH_3 was removed by degassing the sample at 90 °C under He flow

of 70 ml/min for 120 min and then at the rate of 30 ml/min for 150 min. NH_3 desorption of the sample was analyzed by heating the sample at the rate of 10 °C/min from 90 °C to 600 °C. TCD signal was recorded during the NH_3-TPD.

Temperature-programmed reduction (TPR) and temperature-programmed desorption of H_2 (H_2-TPD) were carried out using the apparatus used for NH_3-TPD measurements. The catalyst samples were outgassed at 500 °C for 1 h and then cooled to 50 °C under He flow. TPR profiles were registered while heating the samples from room temperature to 600 °C by 5 °C/min heating rate under flow of 5% H_2/He mixture (20 ml/min). The flow was then switched to He and the samples were cooled to 50 °C. For H_2-TPD, they were heated to 600 °C under He flow (30 ml/min).

Catalyst testing

Citral (mixture of cis- and trans-isomers, Fluka, purity 97%,) hydrogenation experiment was carried out in a semi-batch reactor (500 ml, 4574 model, Parr Instrument Co.) equipped with an electrical heater and temperature controller. Before the reaction, 250 mg of catalysts were reduced in situ at 400 °C for 2 h under the flow of H_2 at 4 bars. Then the reactor was cooled to reaction temperature and stored overnight under H_2 at 2 bars. The reactions were carried out at constant hydrogen pressure of 6 bars at 80 °C with a stirring rate of 600 rpm. The reaction was started by the injection of 0.1 M citral (250 ml ethanol) in to the reactor. Preliminary tests showed that the reaction was kinetically controlled under the condition studied.[10]

Samples taken from the reactor were analyzed with an Agilent Technologies 6890N Network GC System Gas Chromatograph equipped with a flame ionization detector and a capillary column DB-225 (J&W, 30 m, 0.53 mm i.d.). Hydrogenation products of citral were identified by GC-MS technique (Varian Saturn 2000). The compositions of components in the reaction mixture were determined by the internal standardization method.

Yields of different products were calculated as the mole ratio of the product formed divided moles of the citral fed.

Results and Discussion

Catalyst characterization

The physicochemical and textural properties of the catalysts and supports are given in Table 1. Aluminum content of the supports decreased in the following order: Na-Y> Clino. Since the Si/Al ratios were low, these supports were expected to have high concentration of acid sites with low strength.

Pt contents of the catalysts were determined from the initial composition, which was 5.0%. The bimetallic catalysts Sn/(Pt+Sn) mol ratio was 0.02. This gave 0.46 wt% Sn.

The surface area of Na-Y was high as expected. However, the measured surface area for Clino was less than expected; only the surface area of the pores accessible by N_2 molecules was measured. Surface areas and pore volumes were decreased by metal loading. This could be due to the blockage and/or narrowing of some of the pores due to the metal loadings. The shape of the adsorption isotherms remained the same indicating that the crystal structure was preserved after loading.

SEM micrographs of supports showed that the morphologies of the samples were different. They had large and distinct crystallites: Clino ~7 μm and Na-Y ~400 nm.

Table 1. Physicochemical and textural properties of the supports and catalysts.

Catalyst Supports	Si/Al	S_{BET} (m²/g)	V_p^* (cm³/g)	Active Metal** Mean particle size (nm)
Na-Y	2.6	886.1	0.463	-
Pt/Na-Y	2.6	736.3	0.379	17.9
Pt-Sn/Na-Y	2.6	830.2	0.370	15.8
Clino	5.3	43.3	0.065	-
Pt/Clino	5.3	35.0	0.033	5.0
Pt-Sn/Clino	5.3	32.4	0.027	4.1

*Vp: micropore volume.

**: Scherrer equation was used.

The XRD pattern of the catalysts demonstrated that the loading of Pt and Sn did not influence the crystalline structure of Na-Y and Clino as shown in Figure 1. The characteristic peaks of each support were observed in XRD patterns of all monometallic and bimetallic catalysts. Pt peaks were observed at 2θ 39.8° and 46.8° and the peaks of $PtSn_3$ alloy were observed at 2θ 41.6° and 61.8°. Pt active metals on Clino were much smaller than that on the Na-Y, see Table 1. So, a better dispersion of active metal was obtained over Clino. This could be due to their different textural properties.
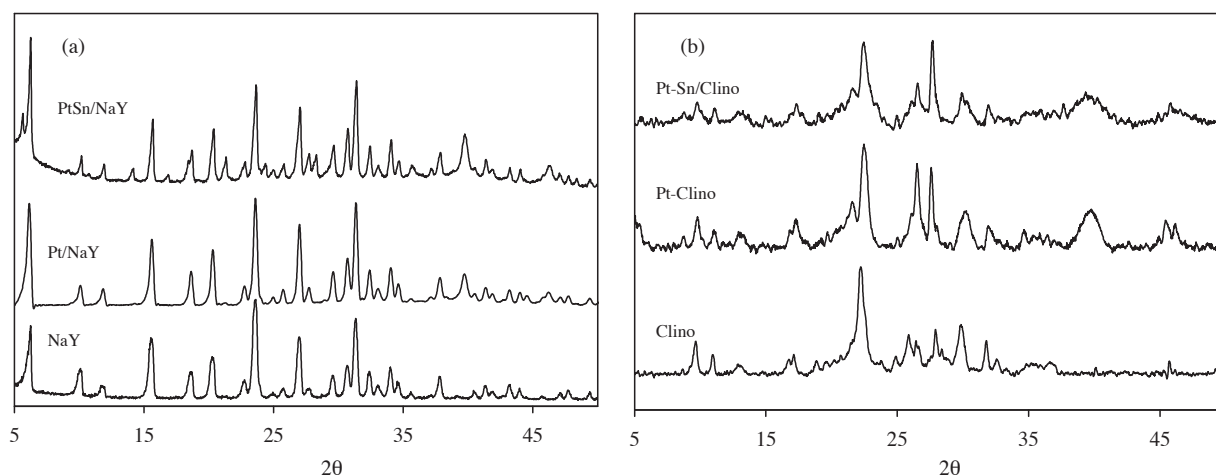
Figure 1. XRD patterns of different supports and catalysts; a) Na-Y and Na-Y supported catalysts b) Clino and Clino supported catalysts.

Acidities of the catalysts determined are given in Figure 2. Active metal loading decreased acidic sites of supports. Over Clino support, Pt and Pt-Sn loading decreased the acidity of the support similarly. However, acidity amount changed differently over Na-Y. Pt-Sn was more acidic than Pt. Among the monometallic and bimetallic catalysts, Pt/Na-Y had the lowest acidity. Pt/Clino and Pt-Sn/Clino had the largest acidity.

H_2-TPD results are given in Figure 3a. The temperature where the maximum H_2 desorption (T_d) was observed changed between 257 and 289 °C over different catalysts. Sn loading for both supports increased T_d. Sn loading decreased the maximum amount of H_2 desorbed over Clino while it increased over Na-Y.

Pt/Clino and Pt-Sn/Na-Y gave the highest desorption amount. This explained the reaction rate observed in Table 2.
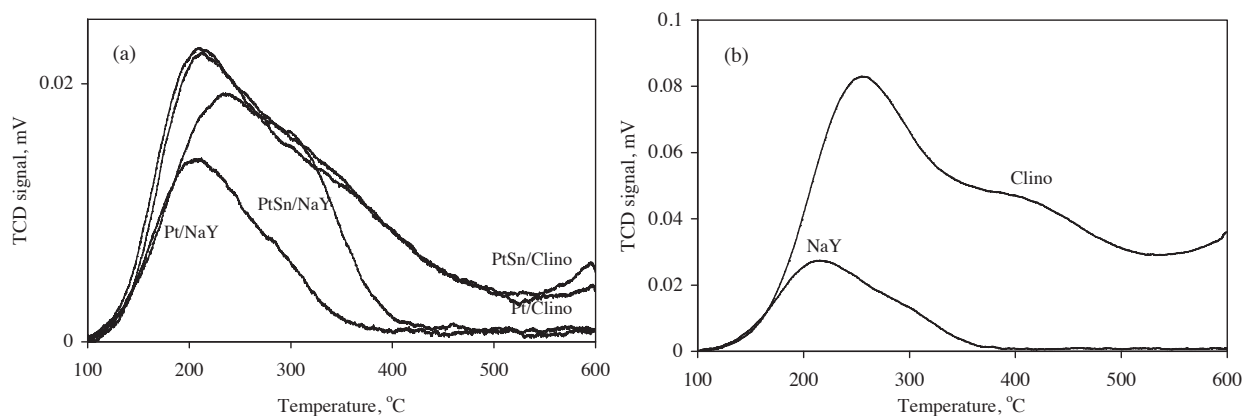
Figure 2. NH₃-TPD of the catalysts (a) and the supports (b).

Table 2. Initial activities and overall conversions observed over the catalysts studied.

	Pt/Na-Y	Pt/Clino	Pt-Sn/Na-Y	Pt-Sn/Clino
X	46.4	59.0	66.7	73.3
$-r_o$, mmol/g$_{Pt}$.s	0.24	0.49	0.57	0.65

Reduction temperatures of different catalysts are given in Figure 3b. The temperature where maximum reduction (T_r) obtained changed differently over the supports studied. Pt was reduced at a lower temperature over Na-Y compared to Clino. Over Clino, T_r increased with Sn addition from 324 to 429 °C while with Na-Y T_r decreased from 260 to 185 °C. So, the reduction of Pt was facilitated over Na-Y. Pt-Sn/Clino was probably not completely reduced during the catalyst reduction step in catalyst testing, as catalyst reduction temperature was 400 °C. The close interaction between the 2 metals could inhibit the reduction of the them.[11] Thus, metal interactions were larger on Clino support.
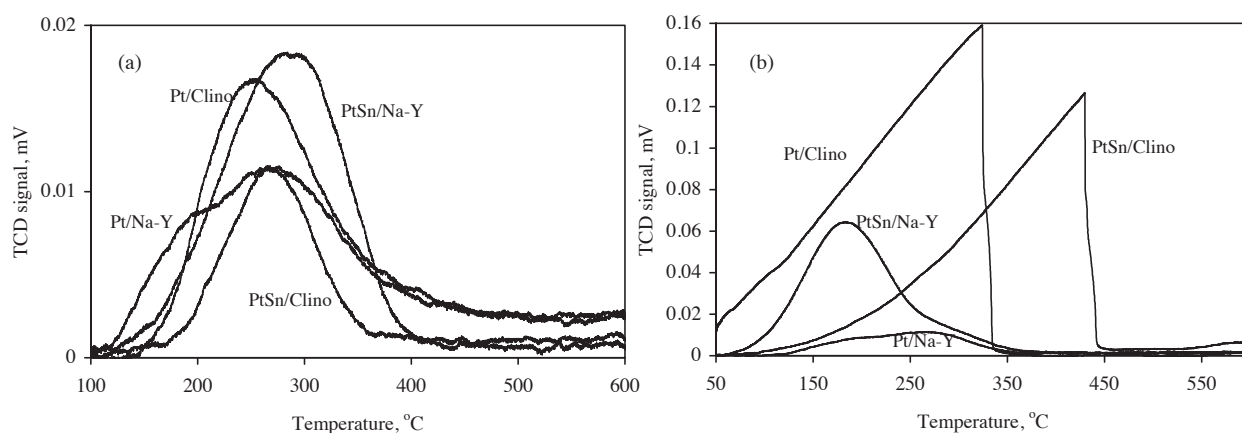

Figure 3. H₂-TPD (a) and H₂-TPR (b) results of different catalysts.

H₂-TPD and TPR results showed that there were different metal interactions with the support and the promoter. The interaction could differ as 2 supports have different surface areas and morphologies. Such interactions could dramatically change the crystallography and the electronic state of the metal particles.[12]

Catalyst testing

Figure 4 shows the product distribution observed over Pt/Na-Y. Citral in the first few minutes of the reaction reacted fast and then declined slowly. The main products formed were citronellal (19.2%), citronellol (3.9%), geraniol+nerol (14.1%), and unidentified+acetals (6.4%). Total amount of unsaturated alcohol formed was 18.0%. It could be suggested that this catalyst had some selectivity toward the hydrogenation of carbonyl bond.
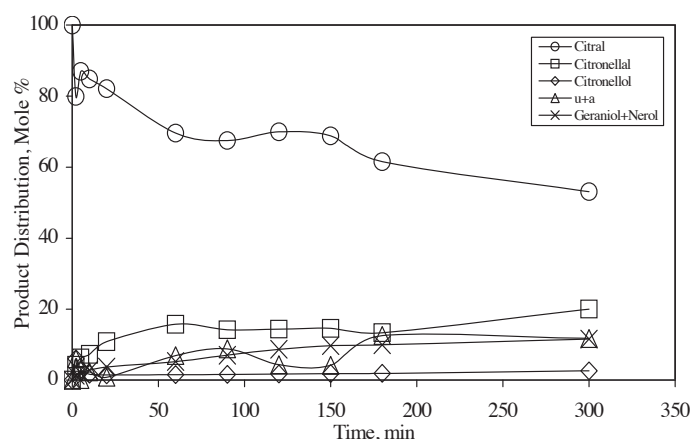
Figure 4.   Product distribution obtained over Pt/Na-Y; u+a: unidentified+acetals.

Figure 5 shows yields of citronellal (Y_{cal}) and unidentified+acetals (Y_{u+a}) over monometallic catalysts. Citronellal was the major product. Higher yield of citronellal was obtained over Pt/Clino (44.7%). Acetals were citronellal and citronellol acetals. Their formation was reversible. They were converted back to citronellal and citral during the reaction. This was the reason for the fluctuations observed in the acetal and citronellal amounts. Larger amount of acetal was formed over Pt/Clino compared to Pt/Na-Y. Their amount decreased at a longer reaction duration reaching similar magnitudes. The difference in the acetal formation could be attributed to the acidity of the catalysts; NH$_3$-TPD showed that Pt/Clino was more acidic than Pt/Na-Y. Acetalization is an acid catalyzed reaction.[13]
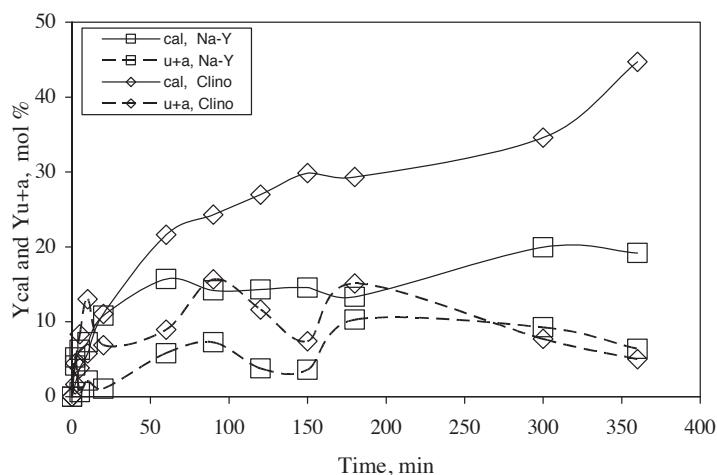

Figure 5. Y_{cal} and Y_{u+a} over Pt/Na-Y and Pt/Clino; cal: citronellal, u+a: unidentified+acetals.

Yields of geraniol+nerol (Y_{g+n}) and citronellol (Y_{col}) for different monometallic Pt catalysts are presented in Figure 6. Pt/Na-Y by far showed higher Y_{g+n}. The maximum Y_{g+n} was 14.1% while Y_{col} was 3.9%. Y_{g+n} increased with the reaction time while Y_{col} made a peak at the beginning of the reaction and then remained constant. Both geraniol and nerol were formed in equal amounts. Pt/Clino gave the maximum Y_{g+n} of 5.1% and Y_{col} of 2.7%. Most of the unsaturated alcohol was nerol. Pt catalysts produced geraniol+nerol more selectively than citronellol. These results showed that Pt selectivity was different over different supports, so the support type affected the activity of Pt differently.

Pt/Clino had smaller active metal particle sites and had higher acidity than Pt/Na-Y. Also TPR results showed that Pt was reduced at higher temperature on Clino than on Na-Y. So there was more metal support interaction on Na-Y than on Clino. This interaction might change the electron distribution on active metal and as a result higher selectivity to unsaturated alcohols was obtained with Pt/Na-Y. Larger active particulates of Pt on surface were less affected by the support as reported by Rodridguez et al.[9]

Aumo et al.[12] investigated Pt/C, Pt/Al$_2$O$_3$, Pt/Polymer fiber catalysts in citral hydrogenation. They reported that higher selectivity to unsaturated alcohols was observed with the catalyst having strong metal support interaction, as it was over Pt/Al$_2$O$_3$. Pt/Al$_2$O$_3$ gave the following maximum yields: 15% citronellal, 34% citronellol, 21% geraniol, and 2% nerol at a conversion of 84%. The influence of metal support interactions has been observed on Pt/SiO$_2$ and Pt/TiO$_2$, which gave the unsaturated alcohols as main products.[14]
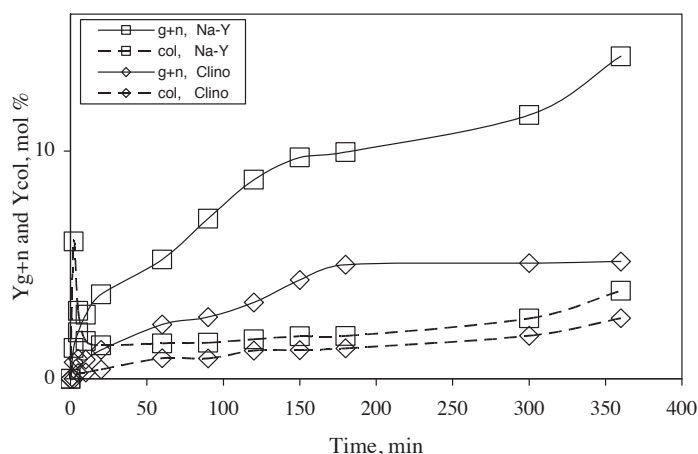

Figure 6. Y_{g+n} and Y_{col} over Pt/Clino and Pt/Na-Y; g+n: geraniol+nerol, col: citronellol.

Hydrogenation of cinnamaldehyde was carried over Pt impregnated (5%) sieve catalysts (H-Beta, H-Y, NH$_4$-Y and H-mordenite), and on Na-MCM-41 and MgO by Hajek et al.[15] It was found that the type of support considerably influenced the catalytic properties. The metal distribution was different over different supports. Over microporous zeolite, selectivity increased with conversion except Pt/Mordenite. Acidity was found to increase activity but it decreased selectivity towards unsaturated alcohol. Pt/H-Y showed higher selectivity than Pt/NH$_4$-Y, 35% compared with 16% at 75% conversion.

Sn loading changed the Y_{cal} and Y_{u+a} of Pt catalysts differently (see Figure 7). The major product was citronellal. Citronellal yield increased with the reaction time up to 300 min and then started to decrease. It was then converted to citronellol. Up to 10% acetal formation was observed. They were converted to citronellal. The highest Y_{cal} over Na-Y and Clino were 52.5% and 39.1%, respectively. Bimetallic catalysts

gave higher Y_{cal} than monometallic catalysts. Slightly lower amount of acetal was formed over bimetallic catalysts.
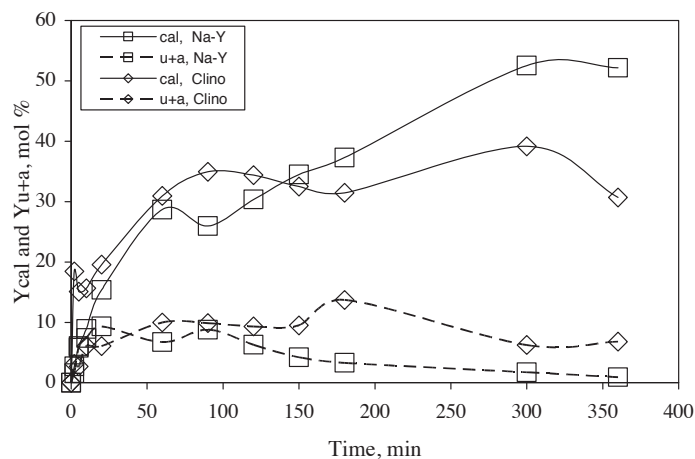
Figure 7. Y_{cal} and Y_{u+a} over Pt-Sn/Na-Y and Pt-Sn/Clino; cal: citronellal, u+a: unidentified+acetals.

Figure 8 shows yields of geraniol+nerol (Y_{g+n}) and citronellol (Y_{col}) for different bimetallic Pt catalysts. Sn improved Y_{g+n} of Pt/Clino from 5.1% to 19.7%. Also Y_{col} increased significantly (from 1.9% to 11.1%). Geraniol and nerol were almost formed in equal amounts. When the yield of unsaturated alcohols was considered together, the total yield achieved was 30.8%. However, the formation of geraniol and nerol decreased; it decreased from 14.1% to 3.0% over Na-Y support. However, Y_{col} increased from 3.5% to 6.8%.

In literature it is reported that active metal properties can be changed upon second metal addition. Second metal addition generally improves selectivity. One explanation for that is the surface polarity of the active metal. Surface polarity of the active metal is reported to increase unsaturated alcohol formation.[5,16,17] Gallezot et al.[5] review reported 2 mechanisms for increase in selectivity upon addition of a promoter: i) the promoter act as electrophilic or Lewis site activating the C=O bond and favoring its adsorption and hydrogenation, or ii) the promoter acts as electron-donor ligand, increasing the electron density of the active metal, which reduces the adsorption of C=C bond and its hydrogenation.

A similar result was obtained by Neri et al.[18] They prepared Pt and Pt-Sn loaded graphite by the coimpregnation method. They found that Sn addition to Pt increased selectivity to unsaturated alcohols, nerol and geraniol from 65% to 90% over graphite support. This was attributed to electrophilic activation of C=O bond by cationic tin on the platinum surface. Monometallic Pt active metal particle size was 3.5 nm and when it was bimetallic its size increased to 7.4 nm.

Pt is much more electronegative than Sn, so surface polarity existed in our catalyst. Increase in selectivity to unsaturated alcohols over Clino support was in agreement with the literature findings. However, Na-Y did not show the expected trend. This could be due to their different properties. Pt-Sn/Clino was more acidic than Pt-Sn/Na-Y. In addition particles over Na-Y were much larger than that on Clino. Also catalysts showed different metal support and promoter interaction as seen with H_2-TPD and TPR. Higher reduction temperatures of Pt-Sn/Clino indicated an interaction between Sn and Pt. Also less H_2 was adsorbed on Pt-Sn/Na-Y than on Pt/Na-Y. This indicated that Sn interacted with the metal. As a result of these differences, higher selectivity were obtained over this catalyst.
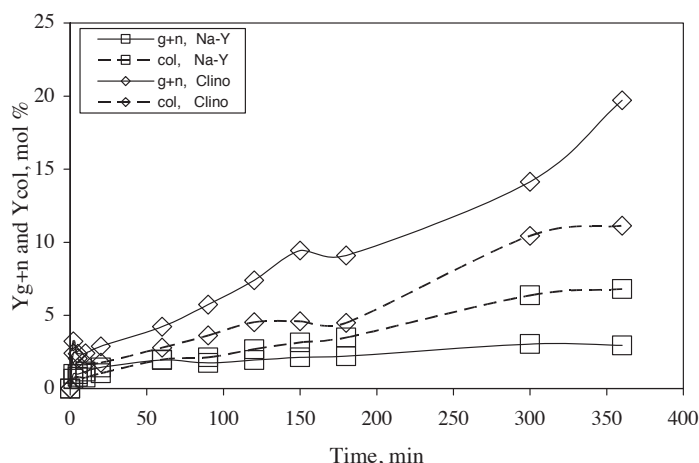
Figure 8. Y_{g+n} and Y_{col} over Pt-Sn/Na-Y and Pt-Sn/Clino; g+n: geraniol+nerol, col: citronellol.

Catalyst activity was measured from initial reaction rates. Overall conversion (X) and initial reaction rates ($-r_o$) calculated for different catalysts are given in Table 2. Bimetallic catalysts gave higher conversions and initial reaction rates compared to monometallic catalysts. Increase of initial reaction rate with promoter addition suggested the existence of synergy between Pt and Sn. This was in line with the literature. Sn addition was reported to increase Ru catalyst activity.[3,19] Bimetallic catalysts showed higher initial catalytic activities. Initial rate changes are in line with H_2-TPD measurements; larger rates were observed for the catalyst giving higher amount of H_2 desorption. It must be also noted that the catalyst with high acidity gave higher initial rates.

Conclusions

Pt and Pt-Sn interacted with Clino and Na-Y differently. Higher interaction was obtained over Na-Y support. Thus, product distribution and activity of the catalyst were influenced by the support material. Monometallic Pt catalysts were selective to citronellal, geraniol and nerol. Geraniol and nerol were more preferably produced than citronellol. Higher selectivity to unsaturated alcohol was observed over Na-Y support. The addition of Sn increased the catalyst activity of monometallic catalysts. This was attributed to the presence of synergy between Pt-Sn. The amount of acetal decreased with bimetallic catalyst. It was noted that Pt-Sn/Clino gave the highest yield of unsaturated alcohols (30.8%). Metal support interaction and promoter active metal interaction increased the unsaturated alcohol formation.

Acknowledgements

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