

Ru-Sn CATALYST - A NEW PROMISING SYSTEM FOR SELECTIVE HYDROGENATION OF A CARBONYL GROUP

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Received October 10, 1996

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1. Introduction

Selective hydrogenation of α,β -unsaturated aldehydes and ketones to corresponding unsaturated alcohols is of considerable interest due to its commercial importance¹⁻⁸ (fine chemicals production - perfume and pharmaceutical industries, food processing). The problem also constitutes a challenging task since the hydrogenation of the C=C bond is thermodynamically favoured over the hydrogenation of the carbonyl group. The unsaturated alcohols are generally obtained by using the reduction of carbonyl compounds with stoichiometric amounts of reducing agents such as hydrides (LiAlH₄, NaBH₄, etc.) or with other specific reagents such as aluminium isopropoxide (Merwein-Ponndorf-Verley reaction)^{9,10}. The heterogeneous catalytic hydrogenation is a more attractive pathway but the regioselectivity of the process must be controlled. Bulk or supported monometallic catalysts like Raney nickel or Pt, Rh, Ru and Pd/support type catalysts are the solids used more usually in the hydrogenation of olefinic bonds¹¹. On the other hand, the selective hydrogenation of α,β -unsaturated carbonyl compounds requires more complex heterogeneous catalytic system¹². A second transition metal (bimetallic catalysts) or a promoter (pseudo-metal) is added to the above-mentioned catalysts in order to enhance the hydrogenation of the C=O bond.

It was found that in selective hydrogenation of unsaturated esters into unsaturated alcohols the carbonyl group of esters is less reactive than that of ketones and aldehydes. This difference in reactivity is due to a weak polarisability and an intrinsic steric hindrance of the C=O bond of esters. As a result, the hydrogenation of esters into alcohols must be performed under severe reaction conditions using similar catalytic systems¹³.

Many efforts have been recently spent to develop a suitable catalytic system for the above-mentioned selective hydrogenation of the C=O bond. The investigated catalysts have been the Group VIII metals^{4-8,14-17} doped with a second metal (Sn, Ge, Ga, Fe). In particular, it has been observed that addition of tin can strongly modify the catalytic properties of ruthenium, giving the unique catalytic system for the selective hydrogenation of the carbonyl group. Electronic and geometric effects have been suggested to explain the improvement in the selectivity to unsaturated alcohols, the respective importance of which is however still discussed^{18,19}. The reaction selectivity has also been influenced by several other parameters such as metal particle size, precursor, support and presence of promoters (especially B)^{20,21}.

2. Preparation of the Ru-Sn catalyst

Ruthenium – tin supported catalysts are prepared by many ways (e.g. coimpregnation, sol-gel, ion exchange, incipient wetness, etc). In this text, attention is paid only to selected aspects of preparation techniques which are specific to this catalytic system.

The modifier is usually added in two different ways: (1) by coimpregnation or (2) by reaction of an organometallic precursor with ruthenium predisposed on a support^{14,22}. The Ru-Sn catalyst supported on alumina was frequently prepared by the „controlled surface reaction” method (CSR)^{2,14,19,20,22}. In brief, the basic principle of this method constitutes reacting parent Ru/alumina catalyst, reduced *in situ* before use, with the desired amount of the organometallic precursor of tin, (C₄H₉)₄Sn, for instance in heptane solution under hydrogen at 353 K. The atomic ratio

ruthenium to the second metal usually varies from 1 : 0.25 to 1 : 2.

It may also be advantageous to use organometallic precursor of ruthenium^{15,18}. The monometallic catalyst was prepared from γ -alumina and ruthenium acetylacetonate by ligand exchange method. The monometallic catalyst was then used as a basis for the bimetallic formulations. The second metal, tin, was introduced by the already mentioned tetrabutyl tin. The use of organic precursor led to very small Ru particles, with a coordination number between Ru atoms of 4.35. The addition of about 0.3 wt % of Sn to the well dispersed Ru sample shifts the catalytic properties towards those of large particles. This effect can be attributed to the preferential occupancy¹⁴ of edge and corner sites (sites with lower coordination) by Sn in bimetallic catalyst, as predicted by the theory of topological segregation. On large ruthenium particles, the addition of tin has only little effect on selectivity. During the coimpregnation of alumina with inorganic precursors, the modifier played a role of nucleation center for Ru, thus also allowing small particles¹⁸ to be formed. Very small Ru particles are sensitive to air, which transforms them to RuO₂ aggregates.

Some Ru-Sn/support catalysts were prepared by the complexing agent-assisted sol-gel method¹³. The method involves dissolving the raw materials of the ruthenium-tin supported catalysts in an organic solvent, with heating if necessary, until a homogeneous solution is obtained. Water is then added to the organic solution. The product of hydrolysis is then coagulated and a gel is formed. After removing the excess of water and organic solvent, the dry gel is ground to a fine powder. The final catalyst is obtained after activation in hydrogen atmosphere with or without calcination. Ruthenium chloride hydrate and ruthenium acetylacetonate were used as the sources of ruthenium. Sources of tin were stannous chloride hydrate, stannic chloride hydrate, and tin ethoxide¹³.

3. Properties of the Ru-Sn catalyst

Burch et al. postulated that tin modifies the electronic properties of small noble metal particles either by interaction with the Sn(II) ion donating electrons to the deficient metal atoms^{23,24} or by incorporation of a few percent metallic Sn as a solid solution into the metal to give the electron rich metal. Galvagno et al. suggested²⁵⁻²⁷ two effects of tin. First, the acidic properties of tin ions activate the carbonyl group which becomes more active than the

C=C double bond. The second effect of tin is related to its electronic interaction with the noble metal, which poisons the active sites responsible for hydrogen activation. Desphanade et al. suggested²⁸ that, in hydrogenation of fatty acids and their esters to unsaturated alcohols, tin ions interact with ruthenium via oxygen to produce selective sites and the tin ion preferentially activates the C=O bond of the ester. Recently Galvagno et al. also investigated^{27,29} the hydrogenation of C=C and C=O groups on ruthenium-tin catalysts. They concluded that the role played by tin in the catalytic activity of ruthenium strongly depends on the organic substrate that is being hydrogenated. In the case of C=C double bonds, the main effect of tin is that of decreasing the number of ruthenium surface atoms. In the case of the C=O group, the tin is present mainly as tin ions and enhances the reactivity of the C=O bond^{29,30}.

There are two possible outcomes depending on the degree of adsorption. In the case of very strong adsorption of the C=O, most of the catalyst surface may be covered by the carboxylic groups^{13,17,18}. In this case, no hydrogenation of the carboxylic group will occur because hydrogen cannot be attached to the surface. In the case of moderate adsorption of the carboxylic group, which permits access of hydrogen and its binding to the catalyst surface, selective hydrogenation of the carboxylic group to alcohol will take place. It is seen that tin increases the affinity of the ruthenium/support catalyst to the carboxylic group. Monometallic ruthenium catalyst without tin does not possess the ability of preserving the C=C bond^{12,22} because the hydrogenated molecule is preferentially adsorbed at its C=C bond. As the tin content increases, the adsorption of the carboxylic group gets stronger. This will usually decrease the catalytic activity of the catalyst system, because the carboxylic group will be strongly adsorbed on the active site of the catalyst, which will prevent hydrogen from reaching the catalyst surface^{13,17,27,29}.

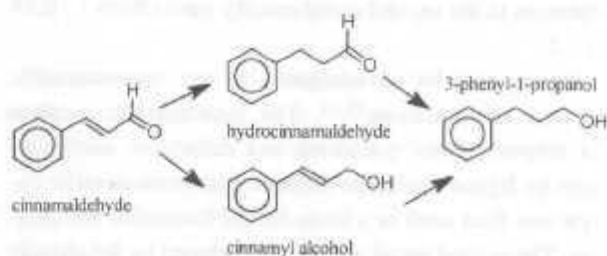
Among the most interesting topics arising from the study are the oxidation state of tin in the catalyst after reduction in hydrogen, the possibility of metal-tin alloy formation, and the extent of the tin-support interaction. These features are greatly affected by the characteristics of the support^{13,14,16,19,20,23}. With regard to the oxidation state of tin, it has been reported that the presence of Sn⁰ after reduction is related to the extent of the metal-support interaction (SMSI). Thus, tin would be stabilized as Sn²⁺ on alumina, whereas¹⁶ it would be reduced to Sn on SiO₂. Furthermore, the tin-support interaction in the case of alumina can lead to the formation of a tin alumina surface shell

that would be able to hinder the sintering of the small metal particles and to influence the behavior of the noble metal atoms in its vicinity. The use of a relatively inert support¹⁶, such as carbon, will allow to discard the possibility of a strong tin-support interaction, facilitating thus the metal-tin interaction. This could lead to the easier formation of metal-tin alloy phases. The highest activity and selectivity are attributed to Ru⁰ sites interacting with Sn²⁺ or Sn⁴⁺ Lewis acid sites^{12,14,17} via oxygen, wherein the Lewis acid preferentially activates C=O, facilitating hydrogen transfer from adjacent Ru-H sites. The existence of such sites could explain the increase in dispersion of ruthenium upon addition of tin. This effect is due to a spacerrole of SnO between Ru⁰ sites. The less abundant Sn⁰ oxidation state is associated¹⁸ with the second type of active sites, with definite evidence of forming an alloy (e.g. Ru₃-Sn₇).

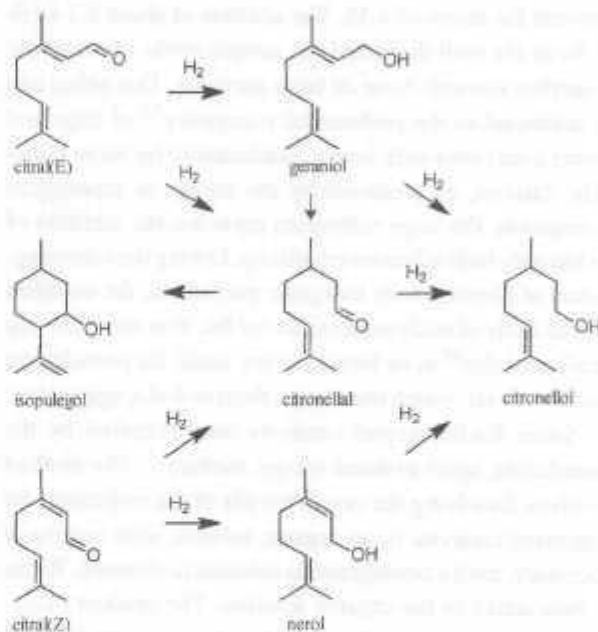
A very promising catalytic system, especially suitable for selective hydrogenation of esters of fatty acids, is based^{12,20,21} on doping the bimetallic Ru-Sn/support catalyst with boron. Narasimhan et al. claimed^{21,31} that in the presence of a Ru-Sn-B/alumina catalyst, the 80 % selectivity to oleyl alcohol is obtained at high conversion (80 %) of methyl oleate at a temperature of 270 °C and a pressure of 4.5 MPa. Such catalysts are commonly prepared by impregnation of tin and ruthenium chlorides on alumina and reduction of these precursors with sodium borohydride. The authors^{21,31} proposed that the active centers are zerovalent ruthenium particles in interaction with tin oxide(s), acting as Lewis acid centers involved in the activation of the carbonyl group. Moreover, the hydrogenation of olefinic bond would be inhibited by a local increase of the electronic state density of the ruthenium particles close to tin species. It was suggested that boron species could interact with ruthenium (with formation of the ruthenium boride Ru₃B) which would favor the specific activation of the hydrogen in the „hydride form“. In other words, the role of boron probably lies in increasing the electronic charge density around Ru, thereby facilitating activation of hydrogen as a hydride^{12,13,21,31}.

4. Utilization of the Ru-Sn catalyst

Hydrogenation of cinnamaldehyde^{1,5,6,15,22,32-34} was studied over supported Ru based catalysts. The influence of bimetallic formulation on activity and selectivity to the desired product, cinnamyl alcohol, was investigated. Addition of Sn as a second metal improved both the activity and selectivity.



Scheme 1. Reaction scheme of hydrogenation of cinnamaldehyde over Ru-Sn catalyst.



Scheme 2. Reaction scheme of hydrogenation of citral over Ru-Sn catalyst

Ru-Sn/alumina showed sustained improvement in selectivity even at higher conversion of the substrate (Scheme 1).

It was shown that in hydrogenation^{1,12,17,22,35-37} of citral (Scheme 2) all the Ru-Sn/support samples prepared were more active and selective to geraniol + nerol than the monometallic catalysts. The selectivity increased e.g. from a value of 35 % on Ru/C to a value of 80 % on Ru-Sn/C. Tin was found to be the only element (among Pb, Ge, Ga, Fe) which changed drastically the product distribution.

Acetophenone was hydrogenated over Ru-Sn/silica catalyst in heterogeneous liquid phase reaction³⁸. The catalytic activity for hydrogenation of acetophenone increased by a factor of 5-500 by Sn addition, showing maximum activity at the surface composition Sn/Ru = 1.5.

Tin has also a very important effect on the selectivity towards the C=O bond hydrogenation of crotonaldehyde^{2,7,8,16,23,39} (or acrolein¹⁹), increasing the production of

crotyl alcohol in respect to the C=C bond hydrogenation that would lead to the production of butyraldehyde.

Hydrogenation of fatty acids or their methyl esters to fatty alcohols is an important industrial process^{13,20,21,31}. There are few catalyst systems reported in literature that can preserve the double bond of the oleic acid or methyl oleate during the process of hydrogenation. However, all these processes are carried out under high pressure (< 15 MPa) and high temperature (250 °C). Recently, Narasimhan et al. showed^{21,31} that methyl oleate could be selectively hydrogenated to oleyl alcohol (9-octadecen-1-ol) by using a mixed ruthenium-tin catalyst under a relatively low pressure.

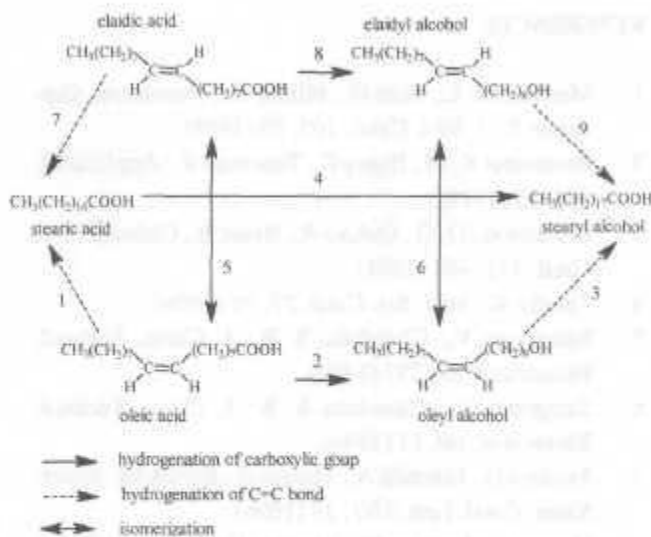
The reactions¹³ that can occur during the hydrogenation of oleic acid are shown in Scheme 3. Parallel reactions 1 and 2 are first step of hydrogenation of oleic acid. The reaction products from reactions 1 and 2 can further be hydrogenated to stearyl alcohol via reactions 3 and 4. Incorporation of tin into the ruthenium-alumina catalyst promotes reaction 2, the hydrogenation of the carboxylic group, and suppresses reaction 1, the hydrogenation of the C=C bond. Isomerization reactions 5 and 6 occur during the reaction. The hydrogenation¹³ of the trans isomer of oleic acid, i.e. elaidic acid, follows similar pathways as described above. Reactions 7 and 8 are the hydrogenation of the C=C bond and carboxylic group, respectively. Elaidic alcohol can be further hydrogenated to stearyl alcohol via reaction 9.

The Ru : Sn ratio 1 : 2 seems to be optimum for the selective hydrogenation of oleic acid to 9-octadecen-1-ol, showing about 95.5 % and 79.1 % of the total alcohol and 9-octadecen-1-ol selectivities, respectively. Beyond this ratio^{13,21,31}, the selectivities for the total alcohol and 9-octadecen-1-ol formation decreases.

Hydrogenation of methyl hexadecanoate, methyl 9-octadecenoate and dimethyl succinate was studied as a function of catalyst composition and various reaction parameters²¹. It was found that the Ru to Sn ratio 1 : 1 gave maximum activity and selectivity for alcohol formation from methyl hexadecanoate and dimethyl succinate. Methyl 9-octadecenoate gave the best yield of 9-octadecen-1-ol at molar ratio of Ru to Sn 1 : 2. The hydrogenation of dimethyl succinate was found to depend delicately on the temperature of the reaction²¹, with the yields of diols reaching a maximum at 200 °C.

5. Conclusions

In this survey, specific properties of Ru-Sn/support type catalysts for the selective hydrogenation of unsaturated



Scheme 3. Reaction scheme of hydrogenation of oleic acid over Ru-Sn catalyst

aldehydes, ketones, acids, fatty acids or their esters to unsaturated alcohols were discussed.

Promotion effect of tin has been attributed to (a) preferential occupancy of the coordination sites by tin which are thought to be responsible for C=C hydrogenation; (b) modification of the electronic properties of the noble metal by electron transfer from tin to the active sites which decreases the likelihood of C=C hydrogenation; (c) activation of the substrate by interaction with tin ions. It was also suggested that application of the CSR method for preparation of bimetallic catalysts tends the promoter to segregate differently on the surface of the noble metal. It was concluded that Sn has a tendency to occupy preferentially the low coordination sites.

On increasing Sn content, the number of Ru surface atom decreases. However, the increase in the specific activity of the C=O group hydrogenation indicates that new and more active sites are formed. It was suggested that preferential hydrogenation of C=O occurs on the sites associated with ionic tin. On these sites the carbonyl group is polarized, facilitating the hydrogen transfer from an adjacent Ru-H site. This is also in agreement with a microstructural characterization which has shown that the Ru-Sn/catalysts are made mainly of metallic Ru particles and ionic tin with a low contents of Sn⁰ particles.

This work was supported by the Grant Agency of the Czech Republic, Grant No. GACR 104/97/0890.

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P. Klusoň and L. Červený (*Department of Organic Technology, Institute of Chemical Technology, Prague*):
Ruthenium-Tin Catalyst – a New Promising System for Selective Hydrogenation of a Carbonyl Group

Unsaturated alcohols are prepared by selective hydrogenation of unsaturated aldehydes, ketones, acids, and their esters. Special attention is paid to the Ru-Sn catalytic systems suitable for such reactions. The Ru-Sn catalyst is usually prepared by co-impregnation, sol-gel method, or so called surface controlled reaction. Interesting topics and specific features regarding this catalyst system are discussed. Role of Sn and its promotion effect on Ru catalytic properties are explained in a separate chapter. These properties are documented on several practical examples (e.g., selective hydrogenation of cinnamaldehyde, crotonaldehyde, oleic acid, etc).