

SELECTIVE HYDROGENATION OF α,β -UNSATURATED ALDEHYDES ON Ru–Sn/TiO₂ CATALYSTSJana ŠPRINGEROVÁ^{a1}, Petr KAČER^{a2}, Jan HÁJEK^b and Libor ČERVENÝ^{a3,*}

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Selective catalytic hydrogenation of unsaturated carbonyl compounds was studied on bimetallic Ru–Sn/TiO₂ catalysts. The catalysts were prepared by a sol-gel method and co-impregnation in order to evaluate selected parameters (amount of the modifying tin, TiO₂ support – commercial, standard sol-gel, modified sol-gel) on their catalytic activity and selectivity. Significant tin effect was proved especially with regard to the positive influence on selectivity. Sol-gel modified TiO₂ was found to be the optimum support. Furthermore, the effect of substrate was studied. The suitability of the catalytic system for hydrogenation of unsaturated aldehydes was proved but it is not suitable for selective hydrogenation of unsaturated ketones.

Keywords: Catalytic hydrogenation; Reductions; Ruthenium–tin catalyst; Sol-gel; Aldehydes; Cinnamaldehyde; Chemoselectivity; Heterogeneous catalysis.

Unsaturated alcohols are important substances in pharmaceutical, perfumery and food industry and are utilized in various organic syntheses^{1–8}. They are prepared by reduction of relevant α,β -unsaturated aldehydes with reducing agents on the basis of complex hydrides as LiBH₄, NaBH₄, *etc.*^{9,10}. Using this type of reduction, almost 100% selectivity was achieved; nevertheless, from the economic and environmental points of view, the necessity to use at least a stoichiometric amount of this agent is a definite disadvantage.

Another possibility to prepare these unsaturated alcohols is utilizing catalytic hydrogenation. On a majority of common catalysts, from both the thermodynamic and kinetic points of view, hydrogenation of the C=C double bond is preferred to hydrogenation of the carbonyl group. Having used group VIII metals¹¹ in the field of catalytic hydrogenation, interesting results were obtained. The metals show even a higher selectivity when modi-

fied by another metal⁴⁻⁸. One of the best possible systems is Ru-Sn where selective hydrogenation of carbonyl function takes place in the presence of a molecule either isolated or conjugated^{12,13}.

This work is dedicated to the study of bimetallic supported catalysts Ru-Sn/TiO₂ with the focus on the effects of various preparation parameters on their catalytic properties, in particular on their activity and selectivity. The effects of the modifying Sn and TiO₂ support (commercial, standard sol-gel, modified sol-gel) were studied. The influence of the substrate (cinnamaldehyde, citronellal) was studied using other effects, where the suitability of this catalytic system for hydrogenation of unsaturated aldehydes with conjugated and isolated C=C and C=O bonds was evaluated.

EXPERIMENTAL

Chemicals

Substrates utilized - cinnamaldehyde and allylacetone (Aldrich, U.S.A.), citronellal (Aroma, Czech Republic). Purity of all substances was higher than 98% (GLC). Hydrogenations were carried out in propan-2-ol (p.a., Penta, Czech Republic). Without any further purifications, the following substances of commercial origin were used for the preparation of catalysts: titanium isopropoxide (97%, Aldrich), RuCl₃·xH₂O ($x \leq 1$) (Aldrich), SnCl₂ (p.a., Aldrich), NaBH₄ (98%, Fluka), electrolytic hydrogen 3.0 (Linde Technoplyn).

Preparation of Catalysts by Sol-Gel Method

Catalysts as well as support were prepared in a three-necked flask equipped with a stirrer and a distillation head with a CaCl₂ stopper. RuCl₃·H₂O (54 mg) and SnCl₂ (42 mg) were dissolved in propan-2-ol (25 ml) and stirred at 343 K for 0.5 h. After complexation of precursors of the active and modifying components a precursor of the support, *i.e.* titanium isopropoxide (10.8 g) in propan-2-ol (25 ml) and 4-hydroxy-4-methyl-2-pentatone (20 g), was added to the solution. After termination of the reaction, hydrolysis with 6 ml distilled water was carried out and coagulation of the solution followed. The gel was left to mature, dried on a rotary vacuum evaporator and chemically reduced with aqueous solution of NaBH₄ (10%). The amount of reduction agent was determined from amount of substance ratio of NaBH₄ and Ru + Sn, *i.e.* $n_{\text{NaBH}_4} : (n_{\text{Ru}} + n_{\text{Sn}})$ have to be 10:1. The catalyst was then calcined in a flow of nitrogen at 473 K for 2 h.

Preparation of TiO₂ Support by Modified Sol-Gel Method

The modification consisted in a rate decrease in hydrolysis of a support precursor and thus achieving its high specific surface. The support was prepared in a flask equipped with a distillation head and CaCl₂ stopper. The preparation proceeded in nitrogen, whose flow stirred the reaction mixture. After the titanium isopropoxide and acetic acid were mixed, immediate precipitation occurred. The precipitate was dissolved in excess of distilled water at 343 K. The volume ratio of components was titanium isopropoxide:AcOH:H₂O = 25:48:150. pH of the produced solution was adjusted with 10% ammonia solution to 3. After coagulation, gel

was matured, dried on a rotary vacuum evaporator and calcined in nitrogen at 473 K for 2 h. The prepared support was further impregnated.

Impregnation

The impregnation was carried out in a three-necked flask equipped with a distillation head with a CaCl₂ stopper. The calculated amount of precursors, *i.e.* RuCl₃·H₂O (54 mg) and SnCl₂ (42 mg) together with methanol (50 ml), was added drop by drop to the suspension of a sol-gel support in methanol. The obtained solution was intensively stirred at the boil for a period of 12 h. Then, after solvent evaporation, the dried catalyst precursor was reduced with a solution of NaBH₄ and dried under nitrogen.

Characterization of Catalysts

Catalysts were characterized by determining the total specific surface by the BET method, the active component surface, the structure of the catalyst support and its particle size (XRD), the content of Ru, Sn, B and Na in catalyst volume (XRF) and by determining the oxidizing state of Ru and Sn (XPS).

Measurement of physical sorption of nitrogen was used for determination of total specific surface. These measurements were carried out on a Pulse Chemisorb 2700 (Micromeritics, U.S.A.) equipped with a TCD. The acquired data were processed by the BET method.

Generally, the method of oxidation of adsorbed hydrogen with a suitable oxidizing agent in a water suspension with potentiometric indication is used to determine the surface of the active metal. On Sn-containing catalysts, such a method cannot be used, as the oxidation of the adsorbed hydrogen proceeds together with oxidation of Sn. Having utilized the work of Paseka¹⁴, the surface of Ru and Sn can be determined electrochemically without the possibility of exact distinguishing the surface portions of Ru and Sn. All above-mentioned results are presented in Table I.

TABLE I
Catalysts characteristics

Catalyst	Theoretical amount of Ru:Sn, wt. %	S _{BET} , m ² /g _{cat}	Ru surface, m ² /g _{Ru}
Ru-Sn/TiO ₂ (SG)	5:0	82.9	2.5 ± 0.6
Ru-Sn/TiO ₂ (SG)	5:1.25	76.6	13.4
Ru-Sn/TiO ₂ (SG)	5:5	44.2 ^a	49.2
Ru-Sn/TiO ₂ (SG)	5:10	44.2 ^a	56.8
Ru-Sn/TiO ₂ (IMP)	5:5	22.0 ^a	442.1
Ru-Sn/TiO ₂ (IMP) ^b	5:5	44.7 ^a	95.6
Ru-Sn/TiO ₂ (IMP) ^c	5:5	281.0 ^a	-

^a Support specific surface. ^b TiO₂ commercial support (Degussa, No.7702). ^c Modified sol-gel support.

X-Ray diffraction is usually used to determine the particle size. The measurement was carried out on a X-ray Diffractometer XRD 3000P (Rich. Seifert & Co., Germany) with Bragg-Brentano geometry and $\text{CoK}\alpha$ -radiation and a graphite monochromator. The particle size was calculated using one point from the most intense line. No diffraction lines corresponding to Ru and Sn were detected and thus the particle size could not be determined. The catalyst seemed to be X-ray amorphous. Crystallographic structure of the TiO_2 support was proved. A dominant crystallographic form was anatase, rutile was apparent as well.

Using an X-ray fluorescence spectrometer, ARL 9400 XP (ART, Switzerland), equipped with the Uniquant program, the metal contents determined. On the Ru-Sn/ TiO_2 catalyst prepared by metal co-impregnation on a sol-gel support, the Ru:Sn ratio was determined (8.1:9.7). Higher content of metals compared with the calculated 5:5 (implied from the preparation procedure) can be attributed to incomplete hydrolysis and condensation during the catalyst preparation.

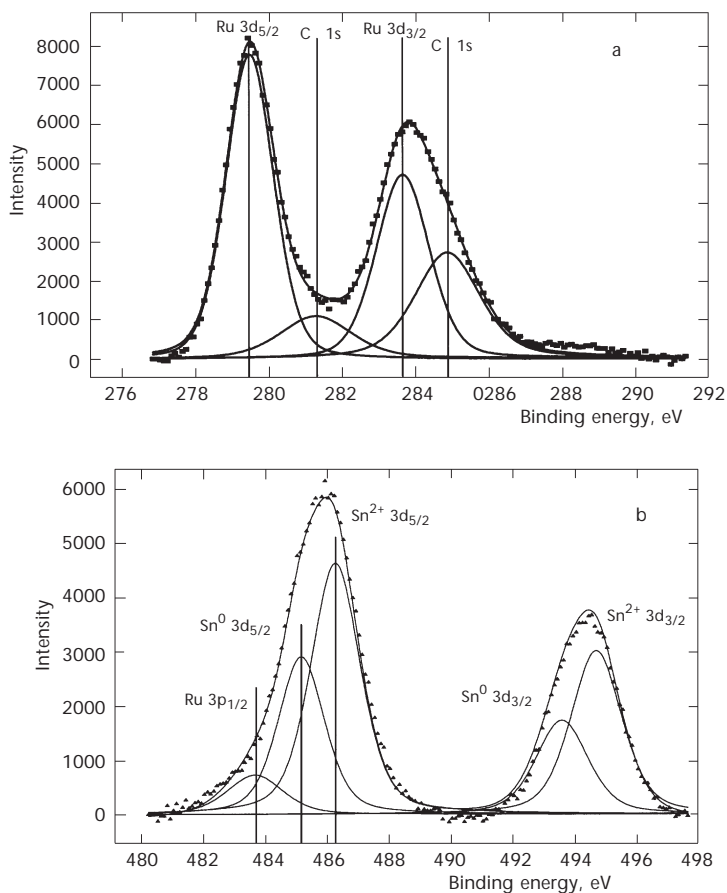


FIG. 1
XPS curve of 3d orbital of Ru (a) and Sn (b) in Ru-Sn/ TiO_2 catalyst

XPS measurements were carried out on an ESCA Perkin Elmer PHI 5400 (U.S.A.) device equipped with MgK α -emitter (1253.6 V). A reduced 5% Ru-5% Sn/TiO₂ prepared by co-impregnation of sol-gel support was used for this analysis. Using this catalyst, the following ratios of atomic concentrations in the surface catalyst layer: Sn/Ru = 1.15; Ru/Ti = 0.96; Sn/Ti = 1.10 were measured. It was found that ruthenium is present as Ru⁰, *i.e.* in the metallic state and tin as Sn⁰ and Sn²⁺ (Fig. 1).

Kinetic Measurements

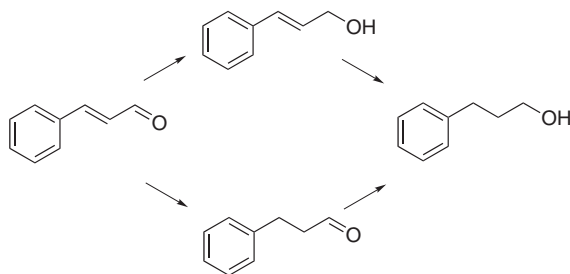
Kinetic measurements were carried out in a PPI 96U-00035 autoclave (Pressure Products Industries, U.S.A.) with total volume 300 ml. Hydrogenation proceeded in liquid phase at a total pressure of 7 MPa and temperature 433 K. Catalyst (200 mg) and propan-2-ol (200 ml) together with substrate (3 g), which were in a small evacuated flask placed near the stirrer, were set to the autoclave. The hydrogenation started after turning on the stirrer, when the flask was broken. All measurements were carried out in the kinetic region, the effect of external diffusion was eliminated by a sufficient stirring, the effect of internal diffusion a finely powdered catalyst. The catalyst was activated prior to the reaction in hydrogen atmosphere at 473 K for 2 h.

Analytical Method

Reaction products were withdrawn in the course of hydrogenation and analyzed using gas chromatography on a Hewlett-Packard 5890 Series II Plus with a flame-ionization detector (FID), equipped with an HP 20M capillary column (length 50 m, ratio 0.25 mm, thickness of the stationary phase 0.32 μ m) and using a temperature program with temperatures ranging between 333–468 K and the overpressure of the carrier gas (N₂) 80 kPa. Using the method of internal standard (n-decane), the content of individual components in the reaction mixture was determined.

RESULTS AND DISCUSSION

3-Phenylprop-2-enal (cinnamaldehyde) was used as the model substance for kinetic testing of the prepared catalysts. Besides cinnamaldehyde, 3,7-dimethyloct-6-enal (citronellal) and hex-5-en-2-one (allylacetone) were used for the study of substrate effects (Scheme 1).



SCHEME 1

Kinetic parameters, utilized to compare catalytic activities and selectivities of the prepared catalysts, were determined at 50% conversion of reactant. The reaction selectivity was defined as $[c_{\text{unsaturated alcohol}} (\%)/\text{conversion} (\%)] 100\%$. The activity of catalysts was evaluated as the reaction rate at 50% conversion of a reactant. Reaction rates were calculated per weight of ruthenium using the theoretical contents instead of real contents, because the real content was measured only for one catalyst.

Characterization of Catalysts

The TiO₂ supports are generally known as low-surface. Table I shows, that by using standard sol-gel method is impossible to achieve higher specific surface. Low specific surface of these catalysts is probably due to easy hydrolysis of support precursor (titanium isopropoxide) on air moisture. Modified sol-gel method leads to high specific surface of catalyst support.

For catalysts prepared by sol-gel method the active metal content increases with increasing amount of modifying metal. It is due to fact, that from principle of used measuring method, the surface of Ru and Sn are determined electrochemically without the possibility of exact distinguishing the surface portions of Ru and Sn. Therefore, with increasing metal content reaction rate decreases.

Effect of Tin Amount

A number of papers¹⁵⁻¹⁸ inform that with increasing amount of tin, the selectivity of hydrogenation of α,β -unsaturated aldehydes increases in favor of the production of unsaturated alcohol. Simultaneously, these works show that the maximum selectivity is achieved at a certain ratio of the active and the modifying metal.

A significant effect of tin was found. The results shown in Table II imply that the presence of Sn significantly influenced the activity of the catalysts, *i.e.* with increasing content of Sn, the activity decreases. Furthermore, it was found that Sn increases the selectivity of the catalysts. The optimal proportion of Ru and Sn, with respect to achieving the maximal selectivity for cinnamaldehyde, was found 5 wt.% of Ru:5 wt.% of Sn.

Galvano *et al.*¹⁶ studied hydrogenation of cinnamaldehyde on Ru-Sn catalysts. They found that with tin increasing content, the catalyst activity decreases and the selectivity to an unsaturated alcohol increases, which is in correspondence with the measured data presented in the present work. Furthermore, they found that if the ratio $\text{Sn}/(\text{Sn} + \text{Ru}) > 0.4$, the sample was

practically inactive. The decrease of the catalytic activity is explained by a decreased H₂ chemisorption on ruthenium.

Burchet *et al.*¹⁵ assumed that Sn modifies electronic properties of catalysts by their interactions with Sn²⁺ ions and by the electron shift to noble metal atoms or by incorporating a part of the metallic tin producing electron-rich particles in the solid solution. Galvagno *et al.*¹⁶ assumed that there are two effects of tin: (i) acid properties of Sn ions activate the carbonyl group, which thus becomes more active than the C=C double bond; (ii) the Sn effect is associated with electron interaction with a noble metal and this interaction leads to poisoning of active Ru sites responsible for hydrogenation of the C=C bond.

Effect of TiO₂ Support

In order to study the effect of TiO₂ support on the catalytic activity and selectivity, three catalysts with 5 wt.% of Ru and 5 wt.% of Sn were prepared. Commercial TiO₂ (Degussa, No. 7702) and TiO₂ prepared by a standard and modified sol-gel method were used as support.

The total specific surface of the support is influenced by the method and conditions of its preparation. The main element affecting the total surface of TiO₂ support is the smooth course of hydrolysis of the support precursor, which is initiated already by air humidity. TiO₂ supports are generally known as having a small surface and enhancement of their surface can be achieved by modifying their preparation. Having compared the total specific surfaces of individual supports, it is apparent that the surface of TiO₂ supports decreases in the order TiO₂ (modified sol-gel method) > TiO₂ (commercial) > TiO₂ (standard sol-gel method). The presented results

TABLE II
Effect of Sn amount on activity and selectivity

Catalyst	Theoretical amount of Ru:Sn, wt. %	Selectivity S_{50} , %	Activity r_{50} mmol/min/g _{Ru}
Ru-Sn/TiO ₂ (SG)	5:0	26.4	159.5
Ru-Sn/TiO ₂ (SG)	5:1.25	52.3	25.6
Ru-Sn/TiO ₂ (SG)	5:5	63.1	11.6
Ru-Sn/TiO ₂ (SG)	5:10	54.3	6.2

(Table III) unambiguously infer that a decrease in the hydrolysis rate of the support precursor led to a significant increase in the total specific surface and thus better catalytic properties are achieved.

Effect of Substrate

5% Ru-5% Sn/TiO₂ catalyst, prepared by co-impregnation of metals on a sol-gel support, was used for the study of substrate effects, whereas cinnamaldehyde and citronellal were used as the substrates. In these molecules, there are more functional groups that can be hydrogenated. In cinnamaldehyde, it is the carbonyl function, C=C double bond and aromatic ring, which are conjugated. In citronellal, the C=C double bond and aldehyd function are conjugated and can be hydrogenated.

Furthermore, hydrogenation of allylacetone was carried out to evaluate the suitability of this catalytic system for selective hydrogenation of unsaturated ketones. On the Ru-Sn/TiO₂ catalyst, both unsaturated aldehydes could be hydrogenated with a relatively high selectivity. A higher selectivity was achieved in hydrogenation of citronellal. Table IV clearly demon-

TABLE III
Comparison of catalysts with various TiO₂ supports

Catalyst	Theoretical amount of Ru:Sn, wt. %	S_{BET} , m ² /g _{cat}	Selectivity S_{50} , %	Activity r_{50} mmol/min/g _{Ru}
Ru-Sn/TiO ₂ (IMP) ^b	5:5	44.7 ^a	55.4	12.9
Ru-Sn/TiO ₂ (IMP)	5:5	22.0 ^a	65.8	16.5
Ru-Sn/TiO ₂ (IMP) ^c	5:5	281.0 ^a	76.3	58.7

^a Support specific surface. ^b TiO₂ commercial support (Degussa, No. 7702). ^c Modified sol-gel support.

TABLE IV
Substrate effect on catalyst 5% Ru-5% Sn/TiO₂

Substrate	Selectivity S_{50} , %	Activity r_{50} mmol/min/g _{Ru}
Cinnamaldehyde	65.8	14.7
Citronellal	95.1	40.0
Allylacetone	0	9.6

strates the significance of the effect of conjugation of the function groups involved. In the unsaturated aldehyde, where C=C and C=O bonds are not conjugated, the aldehyd group could be hydrogenated more selectively.

In hydrogenation of allylacetone, zero selectivity to an unsaturated alcohol was achieved. The presented result is in correspondence with the work of Marinelli *et al.*²¹, who mentioned zero selectivity in hydrogenation of methyl vinyl ketone on ruthenium catalysts.

The literature^{17,18} further shows that the selectivity to unsaturated alcohol increases with increasing number of substituents on the terminal carbon with C=C double bond. Claus²⁰ claims in his work that the steric hindrance due to the presence of substituents causes a significant shift of selectivity, which increases in the order: acrylaldehyde < crotonaldehyde < 3-methylcrotonaldehyde < cinnamaldehyde. The adsorption of substrates is thus strongly dependent on the steric effect of substituents.

CONCLUSIONS

The bimetallic catalyst Ru-Sn/TiO₂ was proved to be suitable for selective hydrogenation of unsaturated aldehydes to corresponding alcohols and *vice versa*, but unsuitable for the selective hydrogenation of unsaturated ketones. A positive effect of tin on the selectivity of the catalysts was proved by kinetic experiments. The optimal ratio of Ru:Sn for achieving the maximal selectivity to an unsaturated alcohol was 5 wt.% of Ru:5 wt.% of Sn. The best TiO₂ support was that with large surface obtained by a modified sol-gel method.

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