CATALYTIC OXOESTERIFICATION
IN GAS PHASE

Václav LOCHAŘ[1], Jaroslav MACHEK and Josef TICHÝ
Department of Physical Chemistry, The University of Pardubice,
CZ–532 10 Pardubice

This paper has the aim to explain the mechanism of oxoesterification of methanol over Mo –Sn –O$_x$ oxide catalyst in the gas phase. Previous studies of similar oxide systems have already proposed a few mechanisms of this reaction. The acid-base, redox properties and catalytic activity in oxoesterification of methanol in the gas phase were investigated for Mo –Sn –O$_x$ oxide catalyst with various Mo/Sn compositions. Reducibility of Mo and Sn species in Mo –Sn –O$_x$ catalyst was studied by temperature-programmed reduction (TPR) in H$_2$ atmosphere. The acidity of this catalyst was studied by means of pyridine adsorption and infrared spectroscopic techniques (FTIR). The temperature dependence of conversion of methanol to methylformate was investigated in the integral flow reactor. The character of surface species resulting from methanol, formaldehyde and methyl formate adsorption was studied by FTIR spectroscopy.

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[1] To whom correspondence should be addressed.

Introduction

Catalytic oxidation of methanol represents an important field of industrial organic chemistry. In oxidation of methanol, practically a number of reactions proceed leading to series of oxidation products. The abundance ratio of products of variable reactions is practically affected by selection of catalyst.

Catalysts based on molybdenum oxide and vanadium oxide are frequently used in selective oxidation reactions due to their high activity and selectivity for partial oxidation products. These catalysts are known to be selective catalysts for oxidation of methanol to formaldehyde [1].

At present, methyl formate is produced on a large scale as an intermediate in the synthesis of formic acid and formamides. However, this ester is a versatile and attractive intermediate for a number of chemicals and may have more applications in the future.

Methyl formate is currently produced by carbonylation of methanol in the liquid phase in the presence of basic catalysts, typically sodium methoxide, at low temperatures and under moderate-to-high CO pressures. Alternative routes to methyl formate have recently been proposed, involving either the gas-phase dehydrogenation of methanol over Cu-based catalysts or the gas-phase oxidation of methanol over various metal oxide catalysts ($Mo-Sn-O_x$ [2] and $V-Ti-O_x$ [3,4] catalysts).

$V-Ti-O_x$ catalysts are very active and selective for the vapor-phase oxidation of methanol to methyl formate. These catalysts require appropriately high surface areas and V loadings. High catalyst contact times are desired too. The behavior observed on increasing either temperature or contact time and data obtained by using dimethoxymethane and water as reagents are consistent with a reaction scheme where methanol is first oxidized to formaldehyde, which can react with gaseous methanol to form dimethoxymethane. Further oxidation of formaldehyde results in the production of first methyl formate and then formic acid and CO. Formic acid is a minor product of methanol oxidation on these catalysts.

$Mo-Sn-O_x$ oxide catalyst has been recognized as promising catalyst for processes in production of methyl formate. It exhibits high catalytic activity in oxidative esterification of methanol in gaseous phase. This fact initiated investigation into properties of this catalyst.

Tests of $Mo-Sn-O_x$ catalysts with different Mo/Sn ratio indicated that the best results for both activity and selectivity for methyl formate were obtained with the Mo/Sn atomic ratio = 3/7 catalyst [2]. The rate of methyl formate formation is practically limited by the oxidation of methanol to formaldehyde, which is controlled by the acidic function of the catalyst. It was proposed that methyl formate is formed *via* formaldehyde as follows

$$2\,CH_3OH \;\rightarrow\; 2\,HCHO \;\rightarrow\; HCOOCH_3$$

It was concluded that the presence of both acidic and basic properties is required to catalyze the reaction [2].

The aim of this work was to determine and explain the influence of redox properties, acidity and catalytic activity of $Mo-Sn-O_x$ oxide catalyst in the course of oxoesterification of methanol in the gas phase. The character of surface species and relationship between them was studied by means of FTIR spectroscopy with the aim to understand the mechanism of oxoesterification of methanol.

These important knowledge together with literature sources have led to suggestion of mechanism of the studied reaction which might be used for production of methyl formate.

Experimental

Preparation of Mo -Sn -O_x Catalyst

Series of $Mo-Sn-O_x$ catalysts with different composition were prepared by evaporation of the water suspension of tin(II) hydroxide with hexaammonium heptamolybdate (tin hydroxide was prepared by precipitation of $SnCl_2$ with ammonia, the precipitate was washed with distilled water several times). The paste obtained was dried at 135 °C for 10 hours. The catalyst was calcined under flowing air at 300 °C for 5 hours and then at 500 °C for 8 hours.

The catalyst composition was verified by chemical analysis (XRF spectrometry), the amorphous structure was proved by X-ray photoelectron spectroscopy, and the specific surface was determined by the BET method.

H_2 -TPR

Reduction of $Mo-Sn-O_x$ catalysts (prior calcined in a flow of oxygen at 450 °C) by hydrogen was monitored in the temperature-programmed reduction apparatus $(20-1000\ °C$, heating rate 10 °C $min^{-1})$. The quartz reactor was charged with 20 mg dry $Mo-Sn-O_x$ catalyst with grain size $0.25-0.5$ mm (content of moisture was determined by DTA-DTG measurement). After leaving the reactor the reduction gas (total flow rate 25 $cm^3\ min^{-1}$, 5 vol. % of H_2 in nitrogen) was passed through a freezing trap kept at -78 °C to remove water. Changes of hydrogen concentration in reduction gas were monitored by means of thermal conductivity detector (TCD).
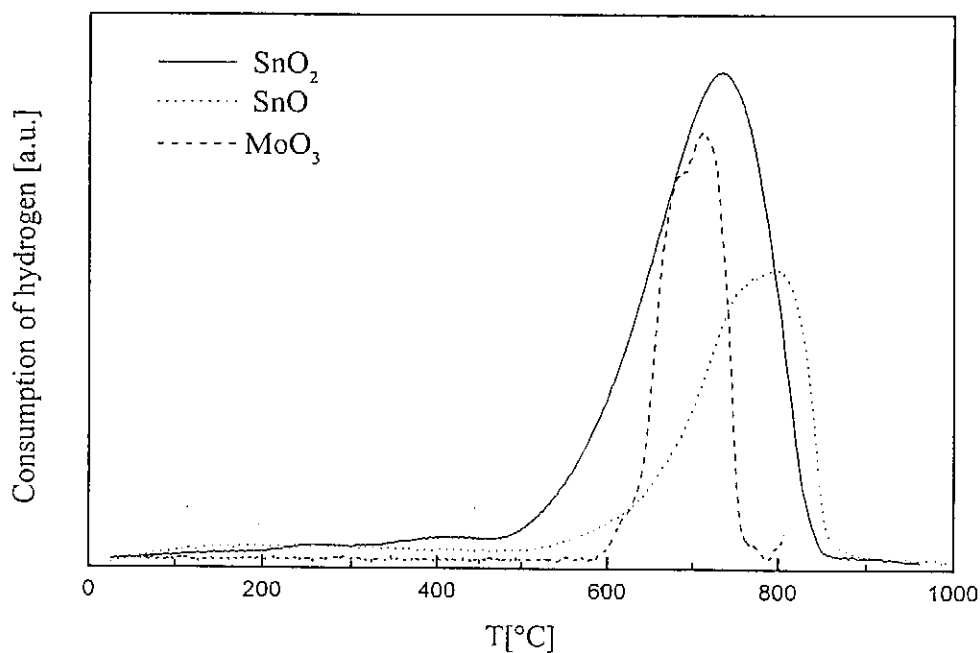
Fig. 1 The H_2-TPR profiles of SnO_2, SnO and MoO_3

FTIR Spectroscopy

The IR spectra were measured in the range from 400 to 4000 cm^{-1} (with resolution 2 cm^{-1}) by using an FTIR spectrometer Protege 460 (Nicolet Instrument Corp.) equipped with an MCT/B detector, which was kept at the temperature of liquid nitrogen. A thin transparent self-supporting wafer of a catalyst (10 – 20 mg per cm^2) was oxidized in air at 400 °C, followed by a short evacuation either at 25 °C or at 400 °C. $Mo-Sn-O_x$ catalysts were treated in pyridine, methanol, formaldehyde and methyl formate (at 1.5 kPa) at various temperatures (25 – 300 °C). The spectra of these components adsorbed at 25 °C were measured for every treatment. The IR spectra were deconvoluted into Gaussian curves.

Testing of Catalytic Activity

The catalytic activity of $Mo-Sn-O_x$ catalysts in oxidative esterification of methanol was measured in an integral flow-through reactor with fixed bed in the temperature range from 100 to 160 °C. Total flow rate of inlet gas mixture was

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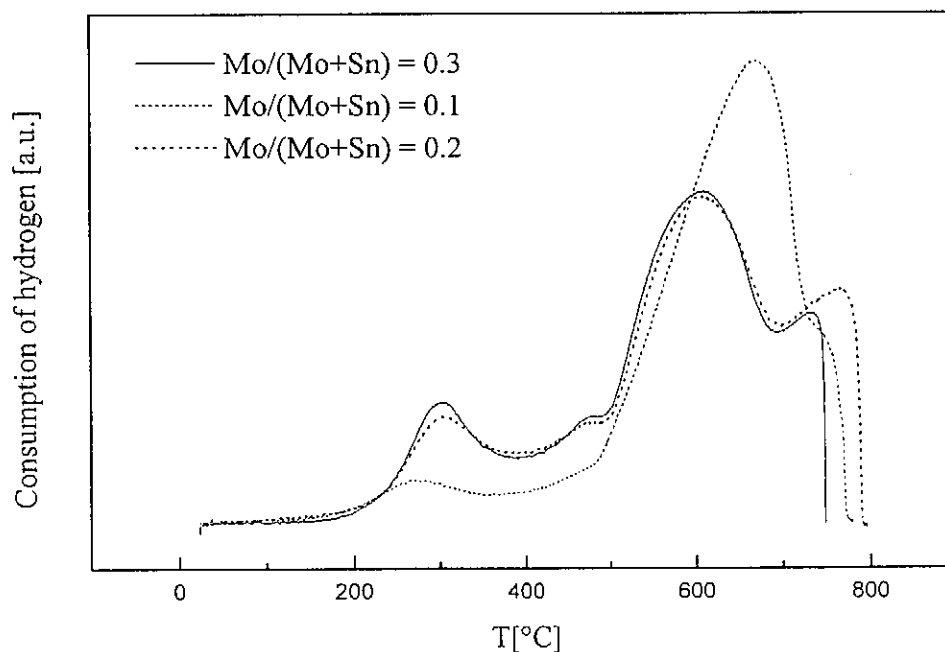
Fig. 2 The H_2-TPR profiles of Mo-Sn-O$_x$ catalysts with various molar ratios Mo/(Mo + Sn)

8 dm^3 hour^{-1} with composition of 6 vol. % methanol, 3 vol. % oxygen and 91 vol. % helium. A 0.25 – 5 g catalyst sample was mixed with the same amount of inert SiC, which prevents local superheating of a catalyst. The composition of reactants was analysed by gas chromatograph CHROM 5 equipped with thermal conductivity detector and packed column (length 250 cm, Porapac Q), connected „on-line" to the catalytic apparatus. The reaction was described by methanol conversion, yield and selectivity of formaldehyde and methyl formate.

Results

Reduction of Mo-Sn-O$_x$ Catalysts by Hydrogen Monitored by H_2-TPR

The reducibility of Mo and Sn species in Mo-Sn-O$_x$ catalysts was studied together with the reducibility of Mo and Sn ions in SnO, SnO$_2$ and MoO$_3$ by temperature-programmed reduction in H$_2$ atmosphere. The H_2-TPR-spectra of SnO, SnO$_2$ and MoO$_3$ (Fig. 1) contained a strong single peak at about 1008 K (SnO$_2$), at about 1053 K (SnO) and at about 963 K (MoO$_3$). SnO$_2$ and SnO are reduced to metal Sn with hydrogen consumption equivalent to four-electron re-
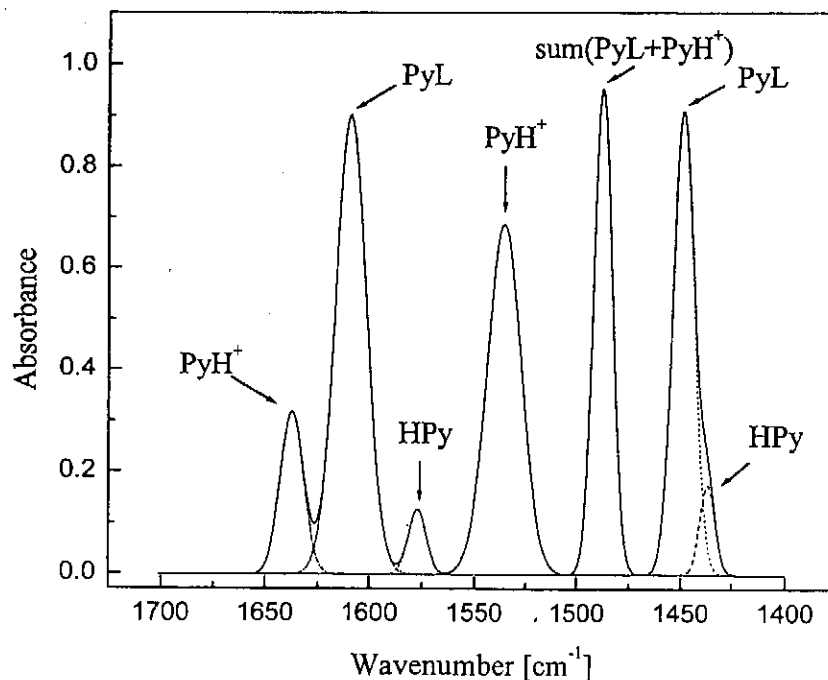
Fig. 3 IR spectra of pyridine adsorbed at room temperature on catalyst with molar ratio Mo/(Mo + Sn) = 0.3

duction (SnO_2) and two-electron reduction (SnO). MoO_3 is reduced to Mo metal. The H_2-TPR-spectra of Mo-Sn-O_x catalysts exhibited three to four reduction peaks (Fig. 2). The position of these peaks changed with changing catalyst composition. According to results of SnO, SnO_2 and MoO_3 reduction and literature source [5] the low temperature peaks at 550 – 823 K corresponded to the reduction of Mo^{6+}, Mo^{5+} surface species. Hydrogen consumption peaks at about 883, 950 K corresponded to the reduction of Sn^{4+} and Sn^{2+} ions.

Acidity of Mo -Sn -O_x Catalysts Determined by means of Pyridin Adsorption and FTIR Spectroscopy

The studies of acidic properties of Mo-Sn-O_x catalysts according to the infrared spectra of adsorbed pyridine indicated the presence of Lewis acid sites (coordinately bonded pyridine) and of Brönsted acid sites (pyridinium ion) (Fig. 3). Absorption bands at 1610 and 1450 cm^{-1} were clasified as Lewis acid site bands. Absorption bands at 1637 and 1537 cm^{-1} were clasified as Brönsted acid site bands [6,7]. The concentration of both centers changed with changing content
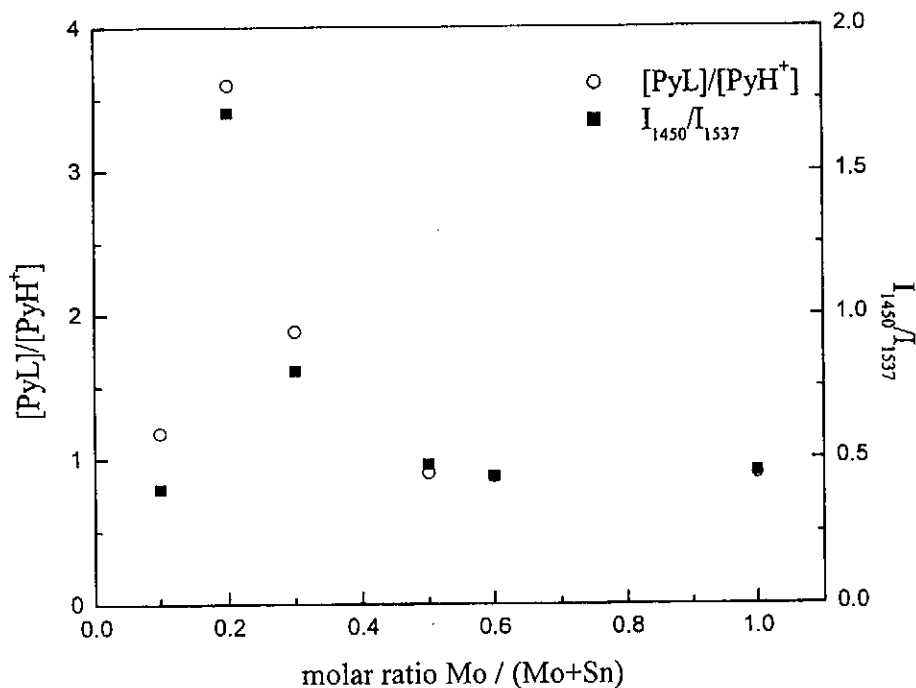
Fig. 4 Changes in the relative number of Lewis to Bronsted acid sites on the $Mo-Sn-O_x$ catalysts with changing molar ratio $Mo/(Mo + Sn)$

of molybdenum in $Mo-Sn-O_x$ catalysts. As proposed by Basila and Katner [8], $[PyL]/[PyH^+]$ ratio was calculated from the equation

$$\frac{[PyL]}{[PyH^+]} = 1.5 \frac{A_{1450}}{A_{1490} - 0.25 A_{1450}}$$

where A is absorbance of the corresponding band. The ratio of numbers of Lewis acid sites to numbers of Brönsted acid sites ($[PyL]/[PyH^+]$) reached a maximum for $Mo/(Mo + Sn) = 2$ (Fig. 4). It was found that acidity (sum$[PyL] + [PyH^+]$) goes through a maximum for $Mo/(Mo + Sn) = 0.4-0.6$.
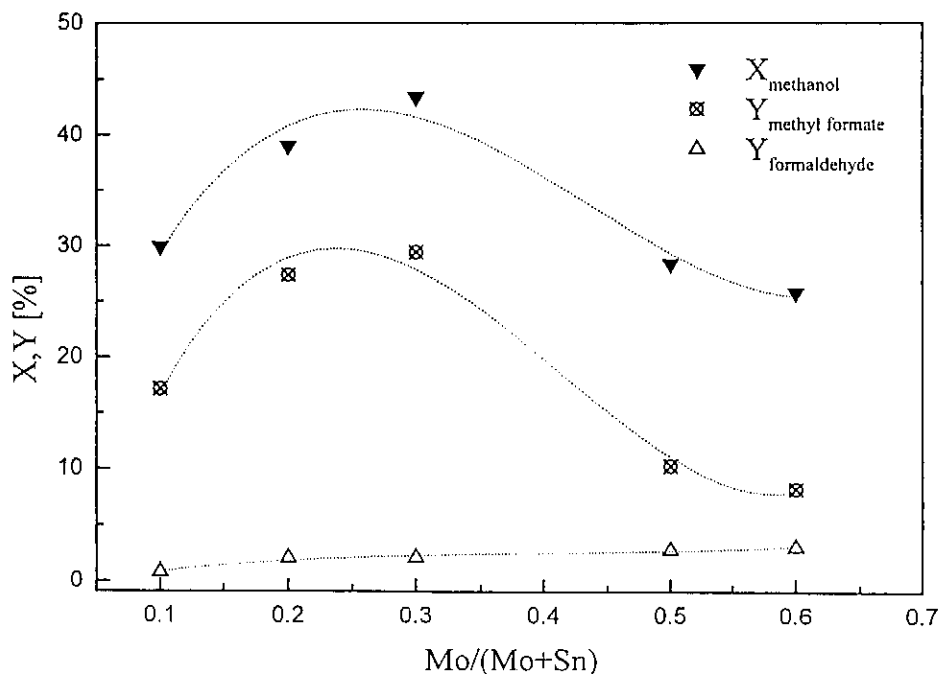
Fig. 5 Effect of content of molybdenum on catalytic activity of Mo-Sn-O$_x$ catalysts in methanol oxidation at 160 °C, X – conversion of methanol, Y – yield of product

Catalytic Activity of Mo -Sn -O$_x$ Catalysts in Oxoesterification of Methanol in the Gas Phase

The temperature dependence of conversion of methanol to methyl formate was studied in the integral flow reactor. It was shown that the main products are formaldehyde, methyl formate, CO, CO_2 and water. The conversion of methanol at 130 and 160 °C increased with Mo content and reached a maximum for Mo/(Mo + Sn) = 0.2 – 0.3, whereupon it decreased with increasing Mo content (Fig. 5). The catalysts with atomic ratio Mo/(Mo + Sn) = 0.2, 0.3 showed the best results for selectivity to methyl formate. During the kinetic measurements (Figs 6, 7) it was proved that the oxidative esterfication of methanol takes place in two steps: oxidation of methanol to formaldehyde and formation of methyl formate from formaldehyde. Formaldehyde is an intermediate and its formation represents the rate-determining step. The conversion of formaldehyde to methyl formate was studied too. The selectivity to methyl formate from formaldehyde is markedly higher (90%) than that from methanol for the catalyst with atomic ratio Mo/(Mo + Sn) = 0.2.
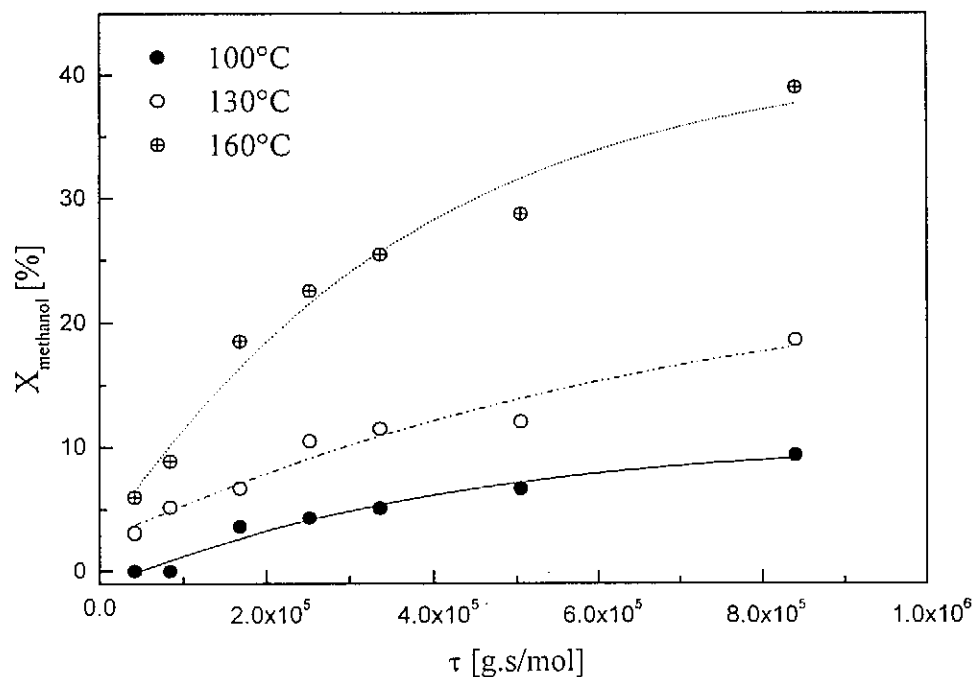
Fig. 6 Effect of time factor (τ) on methanol conversion at 100, 130 and 160 °C

Study of Adsorption of Methanol, Formaldehyde, Methyl Formate and their Surface Species by means of FTIR Spectroscopy

Methanol and its oxidation products form adsorbed species that were characterized spectroscopically on catalyst samples with atomic ratio $Mo/(Mo + Sn)$ = 0.1, 0.2 and 0.3. The reactions of these species were observed directly by FTIR spectroscopy in the same temperature range as that used during the flow reactor experiments.

In the studies of the interaction of methanol with the $Mo-Sn-O_x$ catalysts at room temperature, 130, 160 and 200 °C (and after evacuation at the same temperatures) the infrared spectra of adsorbed methanol indicated the presence of methoxy (absorption bands at 1452 and 1435 cm^{-1}) and formate (absorption bands at 1540, 1375 and 1355 cm^{-1}) species [3]. The surface free hydroxyls react with methanol to give methoxy groups at room temperature (Fig. 8). Oxidation of the surface methoxy groups (I) by heating (100 – 200 °C) in vacuum results in the formation of formate species (II) and formaldehyde. Several types of adsorbed species were identified on the surface of $Mo-Sn-O_x$ catalyst from the IR spectra
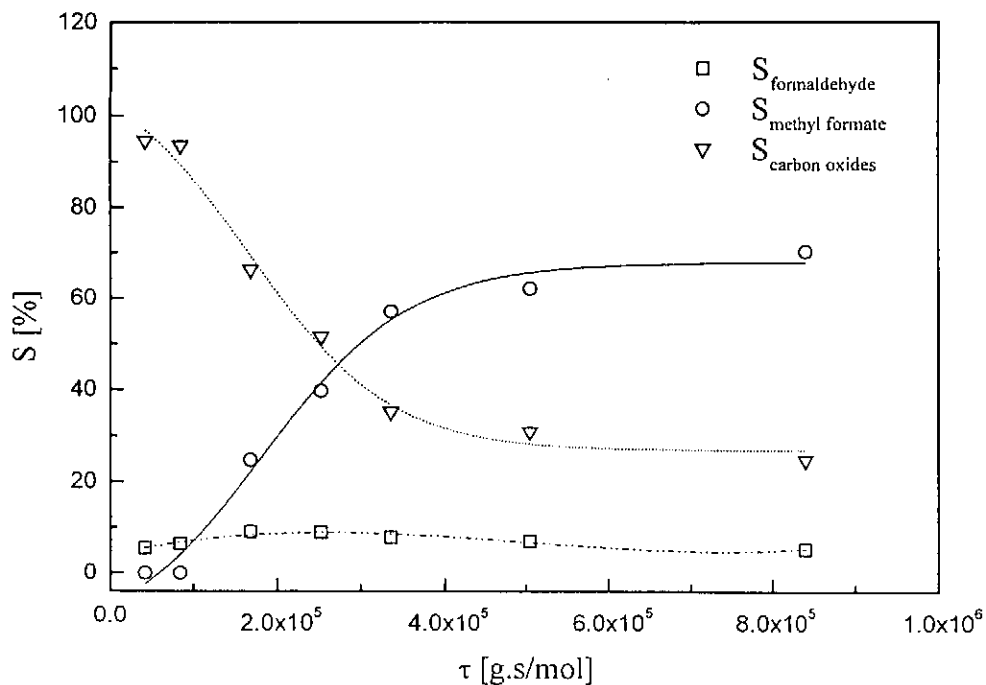
Fig. 7 Effect of time factor (τ) on selectivity (S) to products at 160 °C

of adsorbed formaldehyde [9] (Fig. 9):

1) formaldehyde adsorbed in molecular form due to the formation of hydrogen bonds between its carbonyl oxygen and Brönsted acid sites of $Mo-Sn-O_x$ catalyst (absorption band at 1720 cm^{-1})
2) chemisorbed molecules (coordination bonds on Lewis acid sites, absorption band at 1640 cm^{-1})
3) dioxymethylene species (absorption bands at 1482, 1405 and 1306 cm^{-1}) (III)
4) methoxy and formate groups (absorption bands at 1450, 1433 cm^{-1} and 1540, 1378, 1355 cm^{-1})

In addition to typical absorption bands of methoxy and formate species, bands of molecularly adsorbed methyl formate were observed (a. bands at 1705, 1641 and 1164 cm^{-1}) in the IR spectra of adsorbed methyl formate (Fig. 10).

Discussion

These experimental results together with literature sources have led to suggestion of mechanism of the studied reaction (s – surface, g – gas):
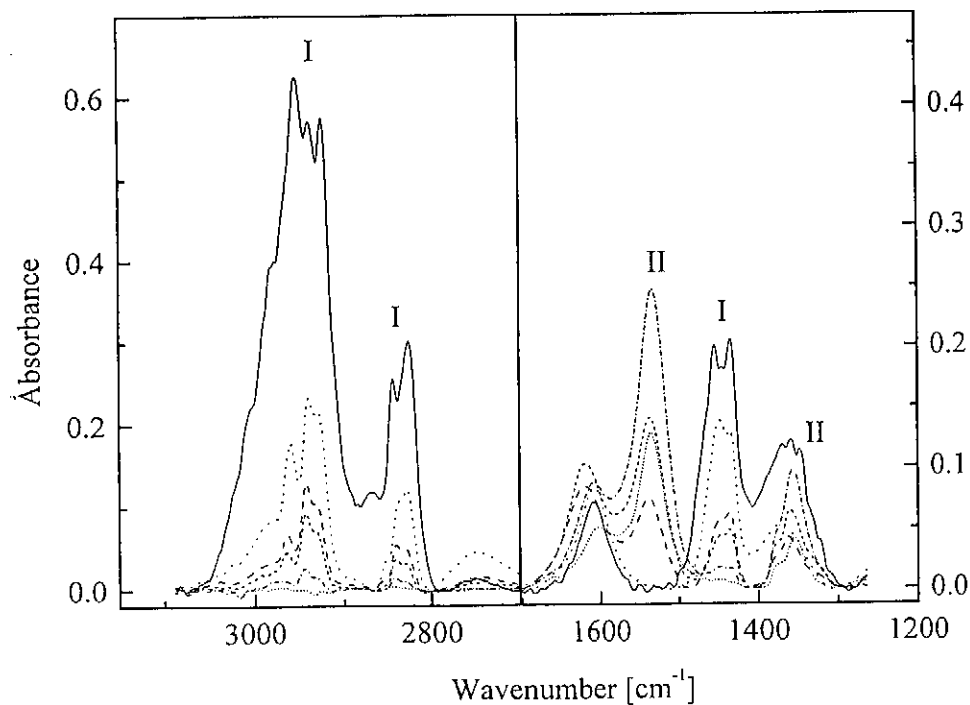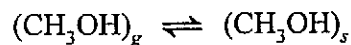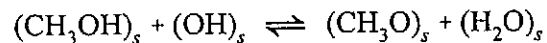
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Fig. 8 IR spectra of methanol adsorbed at room temperature (RT) on catalyst with the molar ratio of Mo/(Mo + Sn) = 0.3 (solid) and evacuated at RT (dot), 373 K (dash), 403 K (short dash), 433 K (short -.-) and 473 K (short dot)
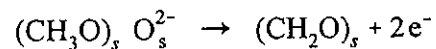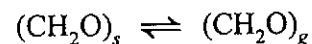
(1) Adsorption of methanol

$$(CH_3OH)_g \rightleftharpoons (CH_3OH)_s$$

(2) Condensation

$$(CH_3OH)_s + (OH)_s \rightleftharpoons (CH_3O)_s + (H_2O)_s$$

(3) Oxidation - redox mechanism

$$(CH_3O)_s \; O_s^{2-} \rightarrow (CH_2O)_s + 2e^-$$

(4) Desorption of formaldehyde
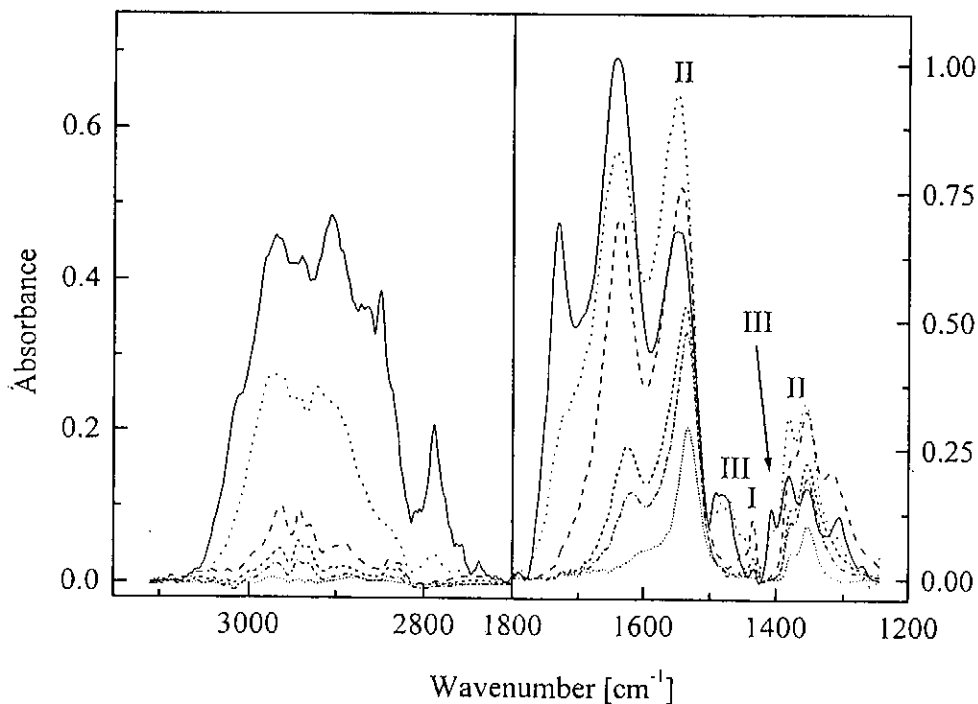
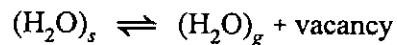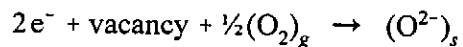$$(CH_2O)_s \rightleftharpoons (CH_2O)_g$$

Fig. 9 IR spectra of formaldehyde adsorbed at room temperature (RT) on catalyst with the molar ratio of Mo/(Mo + Sn) = 0.3 (solid) and evacuated at RT (dot), 373 K (dash), 403 K (short dash), 433 K (short -.-) and 473 K (short dot)
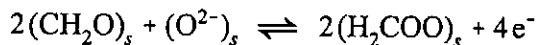
(5) Desorption of water

$$(H_2O)_s \rightleftharpoons (H_2O)_g + vacancy$$

(6) Reoxidation of catalyst

$$2e^- + vacancy + \frac{1}{2}(O_2)_g \rightarrow (O^{2-})_s$$

(7) Formation of dioxymethylene complex

$$2(CH_2O)_s + (O^{2-})_s \rightleftharpoons 2(H_2COO)_s + 4e^-$$

(8) Disproporcionation

$$2(H_2COO)_s + 3e^- \rightleftharpoons (CH_3O)_s + (HCOO)_s + e^- + (O^{2-})_s$$

Fig. 10 IR spectra of methyl formate adsorbed at room temperature (RT) on catalyst with the molar ratio of Mo/(Mo + Sn) = 0.3 (solid) and evacuated at RT (dot), 373 K (dash), 403 K (short dash) and 433 K (short dot)

(9) Esterification

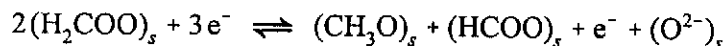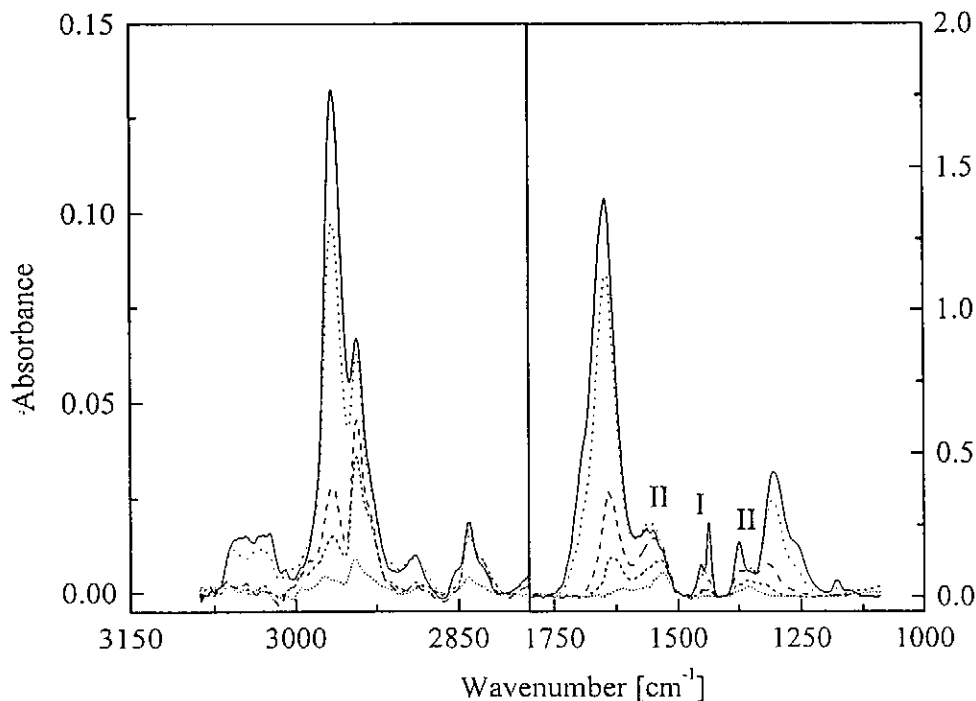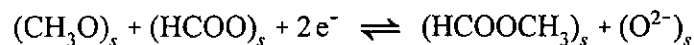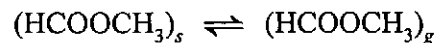$$(CH_3O)_s + (HCOO)_s + 2e^- \rightleftharpoons (HCOOCH_3)_s + (O^{2-})_s$$

(10) Desorption of methylformate

$$(HCOOCH_3)_s \rightleftharpoons (HCOOCH_3)_g$$

Absorption bands at about 3400 cm^{-1} and at 2837 cm^{-1} according to the infrared spectra of adsorbed methanol at room temperatute indicated that the first elementary step of the whole catalytic cycle is adsorption of methanol (1). The following detection of adsorbed water and simultaneous occurrence of surface methoxy groups (I) indicated that the condensation of methanol with free hydroxyls is the second elementary step (2). The increasing of desorption temperature led to the decrease in intensity of the absorption bands corresponding to methoxy groups. Simultaneously, strong complex absorptions appear near 1540

and 1378 cm^{-1}, due to the formation of formate ions (II), at temperatures higher then 100 °C. Absorption bands of adsorbed formaldehyde were also observed at 1640 and 1272 cm^{-1}. The increasing temperature which is necessary for hydrogen abstraction from methoxy groups indicated that this step is an energy demading process. Machiels [1] has shown that hydrogen abstraction from methoxy groups is rate-determining over a molybdate catalyst. This seems to apply to $Mo-Sn-O_x$ catalyst too (3). The products of studied reaction, namely formaldehyde and water were desorbed (4, 5). The last step of methanol oxidation is the reoxidation of catalyst by oxygen from the gas phase (6).

The subsequent dimerization of formaldehyde to methyl formate, which was studied by means of formaldehyde and methyl formate adsorption, is described by equations (7)–(10). Absorption bands at 1482, 1405 and 1306 cm^{-1} in the spectra obtained at room temperature have shown that the formation of dioxymethylene species (7, III) from adsorbed formaldehyde is already fast at room temperature. The simultaneous occurrence of formate and methoxy groups indicated that the next elementary step is the disproporcionation of unstable dioxymethylene species (8). The detection of adsorbed methyl formate has shown that the next step (9) is the esterification of formate ions by surface methoxy groups. The occurrence of methyl formate in the gas phase has revealed that the last elementary step of reaction is the desorption of this ester from the surface of catalyst (10).

These steps (7) – (10) are faster than step (3) because they proceeded at room temperature. In contrast to previeus studies [3,4], methyl formate was formed *via* esterification of formate ions by surface methoxy groups.

The proposed mechanism of oxoesterification of methanol in the gas phase assumed the occurrence of two type of oxygen in thecatalyst. The first oxygen has nucleophilic character and is built in products of redox reaction. The second was involved in the formation of suface species resulting from formaldehyde dimerization to methyl formate.

Conclusion

The present study of oxidative esterification of methanol in gaseous phase proved that:

reduction of $Mo-Sn-O_x$ catalyst proceeded in a way different from the reduction with a simple mixture of SnO_2 and MoO_3; the reduction of $Mo-Sn-O_x$ catalyst does not depend just on experimental conditions (heating rate, variable catalyst load, etc.) but also on the content of both elements and their oxidation state in $Mo-Sn-O_x$ catalyst,

the surface of $Mo-Sn-O_x$ catalyst contained two types of acidic centers, namely Lewis acid sites and Brönsted acid sites; the concentration of both centers changed with changing content of molybdenum in $Mo-Sn-O_x$ catalyst,

the catalysts with Mo/(Mo + Sn) atomic ratio 0.2 and 0.3 showed the best results for activity and selectivity to methyl formate; the oxidative esterification of methanol in gaseous phase takes place in two steps, namely oxidation of methanol to formaldehyde and formation of methyl formate from formaldehyde; formaldehyde is the intermediate and its formation is the rate-determining step,

IR spectra of methanol, formaldehyde and methyl formate adsorbed on $Mo-Sn-O_x$ catalyst indicated the presence of methoxy, dioxymethylene and formate groups; the stability of formate species significantly affects the formation of methyl formate.

These important knowledge together with literature sources have led to suggestion of mechanism of studied reaction which might be used for production of methyl formate.

Acknowledgements

References

[1] Machiels C.J., Sleight A.W.: J. Catal. **76**, 238 (1982).
[2] Ai M.: J. Catal. **77**, 279 (1982).
[3] Busca G., Elmi A.S., Forzatti P.: J. Phys. Chem. **91**, 5263 (1987).
[4] Forzatti P., Tronconi E., Busca G.: Appl. Catal. A: General **157**, 387 (1997).
[5] Arnoldy P., de Jonge J.C.M., Moulijn J.A.: J. Phys. Chem. **89**, 4517 (1985).
[6] Davydov A.A.: React. Kin. Catal. Lett. **19**, 377 (1982).
[7] Davydov A.A., Efremov A.A., Kasumov F.B., Adzhamov K.: React. Kin. Catal. Lett. **18**, 29 (1981).
[8] Basila M.R., Kantner T.R.: J. Phys. Chem. **70**, 1681 (1966).
[9] Busca G., Lorenzelli V.: J. Catal. **66**, 155 (1980).

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