The role of water in ethanol oxidation over SnO_2-supported molybdenum oxides

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The role of water in the oxidation of ethanol to acetic acid on Sn–Mo–O catalysts was studied by catalytic test and FTIR spectroscopy of adsorbed species. The reaction showed a typical behavior of series reactions involving oxidation of ethanol to acetaldehyde and of the latter to acetic acid and CO_2. Addition of water to the feed gas decreased the oxidation rate and significantly increased the selectivity to acetic acid, strongly contributing to decreasing the number of secondary products. FTIR analyses showed that water promotes desorption of ethanol and carboxylates, present as bridging and monodentate species. Decreasing catalytic rate values and increasing selectivity to acetic acid in the presence of water follow from site blocking by hydroxyl groups.

Keywords: water, ethanol, molybdenum, tin

1. Introduction

Acetic acid is produced industrially from ethanol in two stages. Ethanol is first dehydrogenated to acetaldehyde over copper catalysts in gas phase; the aldehyde is then oxidized to acetic acid by manganese complexes in liquid phase. Apart from the use of two reactors, which increases the costs of the process, this suffers from technological limitations such as the deactivation of dehydrogenation catalysts and environmental problems associated with the homogeneous system. Appel et al. [1] pointed out the viability of obtaining acetic acid from ethanol in a single stage, using Pd/Al_2O_3 catalysts. More recently, Allakhverdova et al. [2], using Sn–Mo oxides, synthesized acetic acid, at high yield, directly from ethanol, in a single stage. These authors employed in their experiments high contents of water.

Holstein et al. [3] studying methanol oxidation to formaldehyde over an iron molybdenum catalyst observed that the presence of water led to product inhibition. They suggested that water vapor chemisorbs dissociatively to form hydroxyl groups, which serve to reduce the steady state concentration of methoxy groups on the catalyst surface by promoting methanol desorption. Saleh-Alhamed et al. [4] working on partial oxidation of propene over Sb/Sn/V catalysts suggested that water suppresses the formation of CO_2 by blocking the most active sites that are responsible for complete combustion. However, water also enhances the rate of catalytic oxidation by keeping the catalyst surface at a high oxidation state and preventing the formation of strongly bonded oxygenates. Moro-oka et al. [5] studying the oxidation of propylene by molecular oxygen over Sn–Mo–O showed that H_2O alters the reaction selectivity. They observed that oxidation to acetone depends on the interaction with an active species derived from water molecule, while oxidation to acrolein depends on a species derived from molecular oxygen. Different functions have thus been attributed to water in various reactions.

In this work, we report a FTIR study of the role of water in the synthesis of acetic acid from ethanol over Sn–Mo–O catalysts.

2. Experimental

The Sn–Mo catalyst with molybdenum content equal to 9.2 wt% was prepared by the coprecipitation method [6]. Ammonium hydroxide was added to an aqueous solution of stannic chloride ($SnCl_4$) and ammonium heptamolybate $(NH_4)_2Mo_7O_{24}$ (HMA), yielding hydrated stannic acid ($SnO_2{\cdot}H_2O$). The suspension was evaporated to dryness and the residual solid was dried in oven at 110 °C, and then calcined at 500 °C in a muffle for 16 h. Physical characterizations of this catalyst were already reported in the above cited work.

The catalytic tests were performed in a conventional system with fixed-bed reactor, monitored by on-line gas chromatography. The tests were performed under the following conditions: space velocity 5472, 11520, 28800 and 55584 h^{-1}, temperatures 150, 180, 210, 270 and 300 °C, water partial pressures 0, 30, 54 and 100 Torr, ethanol partial pressure 10 Torr and catalyst mass of 200 mg.

Infrared spectroscopy analyses were performed using a Magna 750-Nicolet (FTIR) apparatus. Catalyst samples of approximately 30 mg were pressed into a thin wafer and used for adsorption of ethanol and acetic acid, respectively. The wafers were treated at 400 °C for 1 h by pulsing O_2

under primary vacuum, evacuated at 10^{-8} Torr at 500 °C for 1 h and cooled to room temperature. Before ethanol or acetic acid adsorption, the wafers were heated up to the adsorption temperature during 30 min in contact with air. The partial pressures of ethanol and acetic acid used in these tests were 10 and 30 Torr, respectively. The adsorption and desorption times were 1 and 2 h, respectively. When desorption was carried out in the presence of steam water, the sample was kept in contact with wet air flowing for 1 h; water was then withdrawn from the feed and the wafer allowed to desorb for more another 2 h in dry air before recording spectra.

3. Results and discussion

Figures 1 and 2 display the selectivity for the products of ethanol oxidation as a function of reaction temperature, in presence of water and without it, respectively. The curves clearly indicate that acetaldehyde is the primary product, which is then oxidized to acetic acid and carbon oxides. The selectivity to acetic acid achieves a maximum at about 270 °C, which is the same either with or without water. Roy et al. [7], in studies related to ethane oxidation using V/Mo/P systems, also observed a maximum at about the same temperature. This probably indicates that above that temperature, the rate of acetic acid combustion became very high compared with the rate of acid formation.

The results show that addition of water to the reaction significantly increases the selectivity to acetic acid. The yield, defined as the molar ratio between produced acetic acid and supplied ethanol, increases with water from 42 to 59% at 270 °C. However, acid formation occurs only above 210 °C. Besides, water decreases the selectivity to CO_2 at low temperatures and also decreases the selectivity to by-products such as ethyl acetate, acrolein, furan, ethyl ether, ethyl formate and methyl acetate. The presence of water strongly contributes to decreasing the number of secondary products.

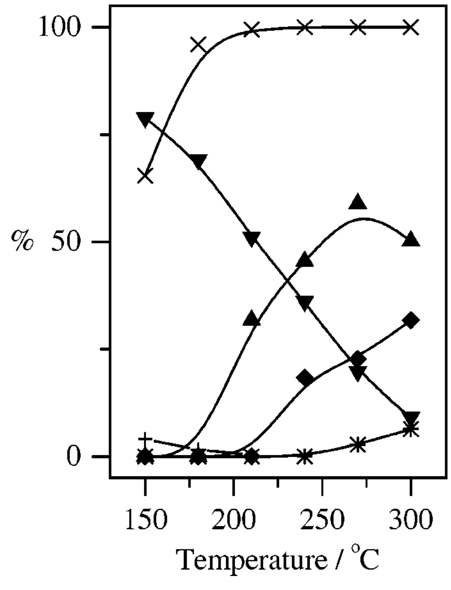

Figure 1. Selectivity in the presence of water vapor as a function of the reaction temperature: (▲) acetic acid, (▼) acetaldehyde, (◆) carbon dioxide, (+) ethyl acetate and (∗) carbon monoxide. (×) Ethanol conversion. The space velocity used was 11520 h^{-1} and the partial pressures of ethanol and water were 10 and 100 Torr, respectively.

The values of ethanol consumption rates obtained in presence of water or without it at 150 °C, are 0.10 and 0.25 μmol/h m^2, respectively. This reduction of reaction rate in the presence of water suggests that water and ethanol compete for the same sites, which should result in smaller ethanol coverage at the surface of the catalyst.

Figure 3 displays the selectivity to the main products as a function of water partial pressure in the feed at 270 °C.

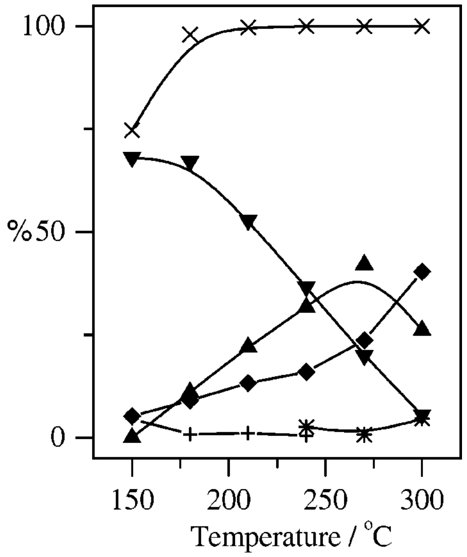

Figure 2. Selectivity as a function of the reaction temperature (without water): (▲) acetic acid, (▼) acetaldehyde, (◆) carbon dioxide, (+) ethyl acetate and (∗) carbon monoxide. (×) Ethanol conversion. The space velocity used was 11520 h^{-1} and the partial pressures of ethanol and water were 10 and 100 Torr, respectively.

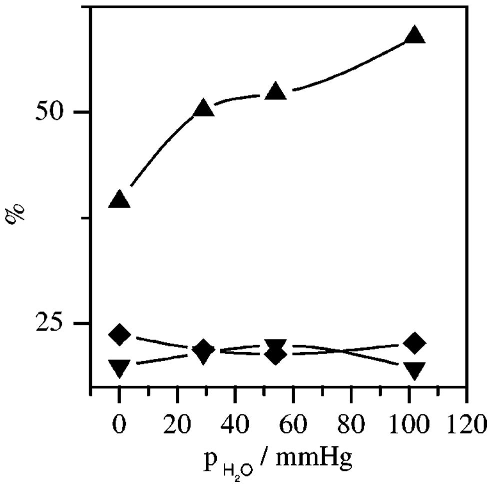

Figure 3. Effect of water vapor pressure on the selectivity of reaction at 270 °C, space velocity of 11520 h^{-1} and 10 Torr ethanol. (▲) Acetic acid, (▼) acetaldehyde and (◆) carbon dioxide.

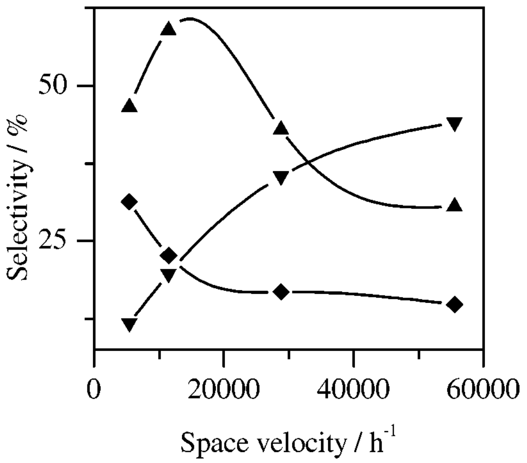

Figure 4. Effect of space velocity on the selectivity of the reaction at 270 °C, 10 Torr ethanol and 100 Torr water. (▲) Acetic acid, (▼) acetaldehyde and (◆) carbon dioxide.

The increase of water pressure promotes an increase in the selectivity to acetic acid. The selectivities to acetaldehyde and CO_2 are not very much influenced at this temperature.

Figure 4 shows the effect of space velocity on the selectivity to the main products of the reaction. It is seen that the selectivity to acetic acid reaches a maximum at 11520 h^{-1}. Increase of space velocity promotes an increase in selectivity to acetaldehyde and a decrease in relation to CO_2. These results are in accordance with those expected for a network of oxidation reactions in series.

Figure 5 displays the infrared spectra recorded in the 2000–1000 cm^{-1} range after adsorption of ethanol on Sn–Mo oxides. Spectra (a) and (b) refer to adsorption at 25 °C followed by purge in the presence of dry air and wet air, respectively. Absorption bands were observed at 1626, 1450, 1390, 1266, 1089 and 1042 cm^{-1}, which were attributed to water and adsorbed ethoxide. The latter bands are strongly weakened on spectrum (b), confirming that water displaces adsorbed ethanol from the surface at low temperature.

Spectra (c) and (d) (figure 5) are related to ethanol adsorbed at 200 °C and desorbed at the same temperature with dry air and wet air, respectively; absorption bands are observed at 1712, 1527, 1435, 1387 and 1320 cm^{-1}. The first one could be assigned to the carbonyl stretching mode from adsorbed acetaldehyde. The bands at 1527, 1435, 1387 and 1320 cm^{-1} were attributed to carboxylate species, in agreement with Zaki et al. [8]. In accordance, we have observed almost the same spectrum (figure 5(g)) after adsorption of acetic acid on Sn–Mo oxides at this same temperature. The bands at 1527 and 1435 cm^{-1} were assigned to asymmetric and symmetric $–CO_2$ stretching modes of bridging carboxylates. The other two bands at 1387 and 1320 cm^{-1} might be attributed to symmetric stretching modes of monodentate carboxylates; tentatively, the weak band at 1712 cm^{-1} could then correspond to the asymmetric stretching mode of these species. Comparison between spectra (c) and (d) (figure 5) shows a decrease of the intensity of all these bands, indicating that water displaces carboxylate species from the surface. However, such an effect is smaller than that observed with ethanol and suggests, in agreement with our not detecting acetic acid among reaction products at 200 °C, that carboxylate precursors are strongly bonded to the catalyst surface and desorb only at higher temperature.

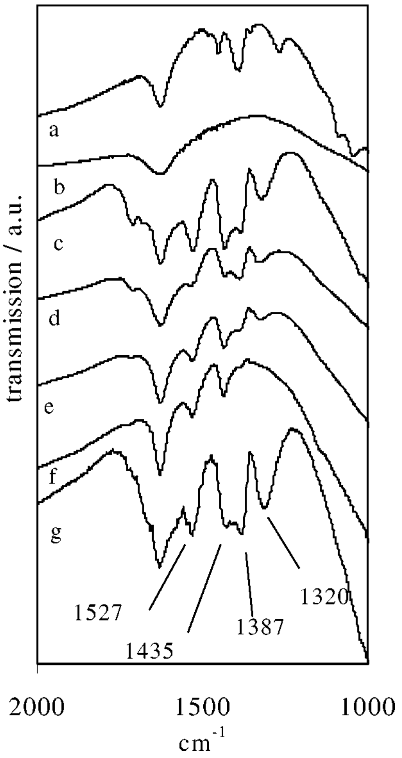

Figure 5. Infrared spectra after adsorption of ethanol at 25 °C and desorption in air (a), 25 °C and desorption in air with steam water (b), 200 °C and desorption at 200 °C in air (c), 200 °C and desorption at 200 °C in air with steam water (d), 270 °C and desorption in air (e), 270 °C and desorption in air with steam water (f). Infrared spectra after adsorption of acetic acid at room temperature and desorption at 200 °C (g).

Figure 5 (e) and (f) display the spectra after adsorption at 270 °C and desorption in dry and wet air, respectively. Main absorption bands are observed at 1626, 1527 and 1435 cm^{-1}, and smaller bands at 1387 and 1320 cm^{-1}, which are very weak in spectrum (f); these results are in agreement with the greater thermal stability of bridging species. The strong weakening of the two bands at 1387 and 1320 cm^{-1} in spectrum (f), suggests that desorption of monodentate species at this temperature is yet favored by water.

In their study of ethanol oxidation, Nagal et al. [9] proposed that acetic acid was obtained from monodentate carboxylate species. The results presented here show that, while oxidation products of acetaldehyde are not observed in the gas phase at 200 °C, the addition of water to the feed decreases the ratio between bridging and monodentate carboxylate species. It is probable that water adsorbed on the surface would hinder the formation of bridging species, since this reaction needs two neighbor sites. At 270 °C, however, only the infrared bands of bridging species were observed after desorption with wet air. This was attributed to the lower thermal stability of monodentate species. In accordance, we note that the highest selectivity to acid occurs at this temperature, while bridging species stick at the surface.

Two factors may then be invoked to explain the increase of selectivity towards acetic acid after addition of water to the stream. On the one hand, site blocking by hydroxyl groups precludes the formation of bridging species from monodentate ones, thus avoiding the degradation reaction channel. On the other hand, water induces desorption of adsorbed species, which strongly reduces superficial concentrations and helps to prevent formation of by-products.

4. Conclusion

The oxidation of ethanol to acetic acid over Sn–Mo oxides presents a typical behavior of series reactions involving the oxidation of ethanol to acetaldehyde and of the latter to acetic acid and CO_2. The catalytic results show that the presence of water in the stream decreases ethanol conversion but increases selectivity to acetic acid. The FTIR study indicates that this behavior can be due to competition between water and ethanol or adsorbed species for the same catalytic sites. Decreasing the concentration of superficial species on the catalyst leads to decreasing conversion and, more drastically, to decreasing secondary reaction rates, hindering formation of by-products. Inhibition of bridging carboxylates in favor of monodentate species enhances the selectivity of the catalyst towards acetic acid.

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References

[1] L.G. Appel, C. Moraes, S.E. Pereira, Z. Guimarães and P.R.S. Medeiros, Brasil PI 8901776; 14/04/89 Rio de Janeiro, INPI (1989).
[2] N.Kh. Allakhverdova, K.Y. Adzhamov and T.G. Alkhazov, Kinet. Katal. 33 (1992) 327.
[3] W.L. Holstein and C.J. Machiels, J. Catal. 162 (1996) 118.
[4] Y.A. Saleh-Alhamed, R.R. Hudgins and P.L. Silveston, J. Catal. 161 (1996) 430.
[5] Y. Moro-oka, Y. Takita and A. Ozaki, J. Catal. 27 (1972) 177.
[6] P.R.S. Medeiros, F. Gonçalves, J.G. Eon and L.G. Appel, Appl. Catal. A 193 (2000) 195.
[7] M. Roy, M. Gubelmann-Bonneau, H. Ponceblanc and J.C. Volta, Catal. Lett. 42 (1996) 93.
[8] M.I. Zaki and N. Sheppard, J. Catal. 80 (1983) 114.
[9] M. Nagal and R.D. Gonzalez, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 5251.