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Gas–solid oxidations with RuO_2–TiO_2 and RuO_2–SiO_2 membranes

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Abstract

The activity of the RuO_2–TiO_2 and RuO_2–SiO_2 membrane catalysts in oxidation with air of the isopropylic alcohol was determined at temperatures ranging from 40 to 120°C. The RuO_2–TiO_2 and RuO_2–SiO_2 membranes were prepared by the sol–gel process and supported on microporous glass membranes. The catalysts were characterized by scanning electron microscopy, IR spectroscopy and X-ray diffraction studies.

1. Introduction

Development and commercialization of good quality inorganic membranes have favoured a great diversification of the catalytic membrane reactors applications [1–6].

First studies concerning integrating membrane and catalytic functions have shown that palladium and palladium alloy membranes are effective catalysts in hydrogenation and dehydrogenation reactions [5–9]. Later, an important number of studies in the catalysis work has focused on hydrogen transfer and there has been a limited amount of work on oxygen transfer through ceramic or metal membranes [10–12]. In a approach to transfer oxygen through a membrane, Gryaznov et al. [11] studied the oxidation of hydrocarbons and alcohols with a silver membrane.

The most recent applications of the ceramic membrane reactors have involved the use of sol–gel alumina, silica, titania and zirconia membranes. By the sol–gel process, catalysts with a high activity and selectivity can be obtained through incorporation of the active metal in the sol during the gelation [13,14].

In this work the sol–gel procedure has been chosen to produce the RuO_2–TiO_2 and RuO_2–SiO_2 thin films supported on microporous glass membranes. The catalytically active membranes used in the reactor ensure the activation of the chemical process and, at the same time, intermediate and control the contact between the reactants in the oxidation of isopropylic alcohol.

2. Experimental

TiO_2 sol was prepared by partial hydrolysis of titan(IV) isopropylate (TiOT) in the presence of water resulting from an esterification reaction between propylic alcohol (in excess) and acetic acid (pH = 4). SiO_2 sol was prepared by the

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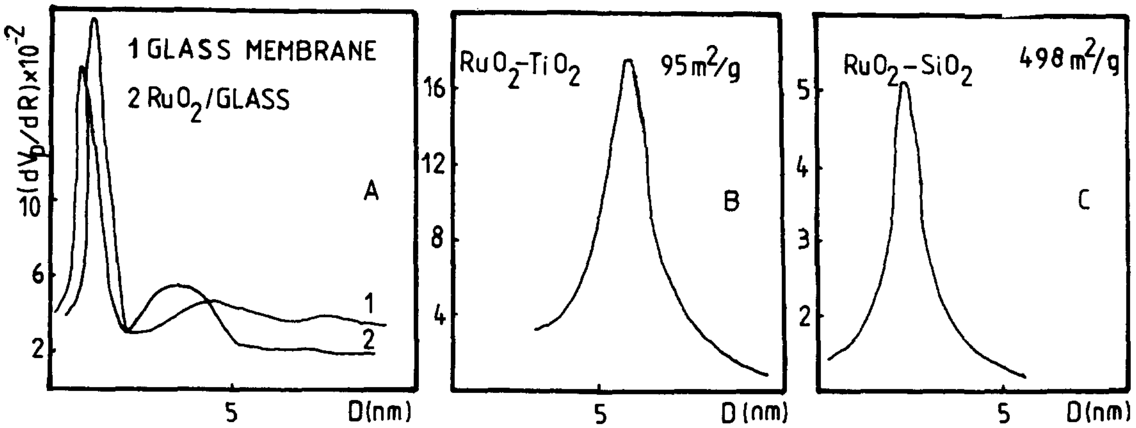

Fig. 1. Pore distribution for catalytic membranes and powder.

hydrolysis of tetraethoxysilane (TEOS) in ethylene glycol, water and HCl (pH = 3). Solutions of $RuCl_3 \cdot 3H_2O$ in propylic alcohol and ethylene glycol respectively, were added to the TiOT and TEOS derived sols. The sols, with adapted binder/plasticizer, were deposited, by spin coating on microporous glass support. The deposits were then dried and calcinated at 600°C. In such a way, RuO_2–TiO_2 and RuO_2–SiO_2 membranes with 35.2 wt.-% and 10.4 wt.-% Ru, respectively, were obtained.

Other catalysts obtained by impregnation of glass membrane (EZP = 5.6) with an acidic (HCl) $RuCl_3$ solution (pH = 1), drying and calcination (600°C) were prepared too. These RuO_2 catalytic membranes have been compared to previous ones.

The specific surface area and pore size distributions (RuO_2–TiO_2, RuO_2–SiO_2; prepared in the same conditions as the membranes) were determined from nitrogen adsorption–desorption isotherms. The pore size distributions of the RuO_2/glass membrane, before and after catalytic layer deposition, were also determined. The RuO_2–TiO_2 and RuO_2–SiO_2 sol–gel were characterized by IR spectroscopy and X-ray diffraction and the derived membranes by scanning electron microscopy.

Measurements of oxygen and isopropylic alcohol permeation rates and effective diffusion coefficients were carried out by introducing air or alcohol vapour in the argon stream to the lower side of the reactor and argon at the upper side (40–120°C).

After the system attained steady state, the oxygen concentration at the outlet of the permeation side was determined by means of gas chromatography.

Oxidation of isopropylic alcohol in the gas phase (vaporization in argon stream) was performed in a catalytic membrane reactor (isothermal conditions). The reaction took place under a difference of pressure between the two sides of the membrane ranging within 0–1 atm at low temperature (40–100°C). The overall molar flow rate and the gas composition were maintained constant throughout the reaction. Air was used as oxidizing agent.

3. Results and discussion

The membranes and powders pore volume distribution are shown in Fig. 1 (A,B,C). The results revealed a microporous structure of the support with a non negligible contribution of the pores with a diameter higher than 1 nm (40%). After the impregnation, this structure is insignificantly modified (Fig. 1A). The RuO_2–TiO_2 powder exhibits a monomodal distribution with a maximum around 6 nm and a surface area of 95 m^2/g while in the RuO_2–SiO_2 powder the maximum is around 2 nm and the surface area 498 m^2/g.

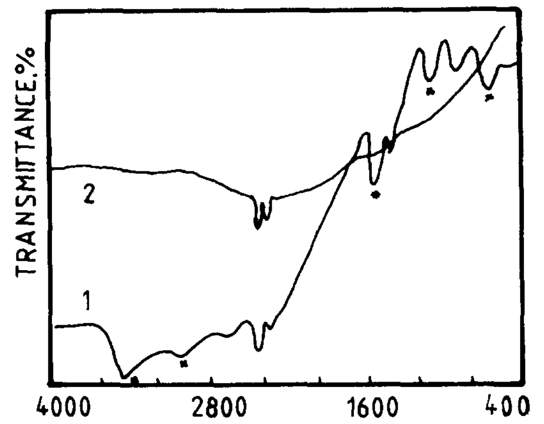

Fig. 2. IR spectra of the RuO_2–TiO_2 gels thermally treated at: (1) 80°C; (2) 600°C.

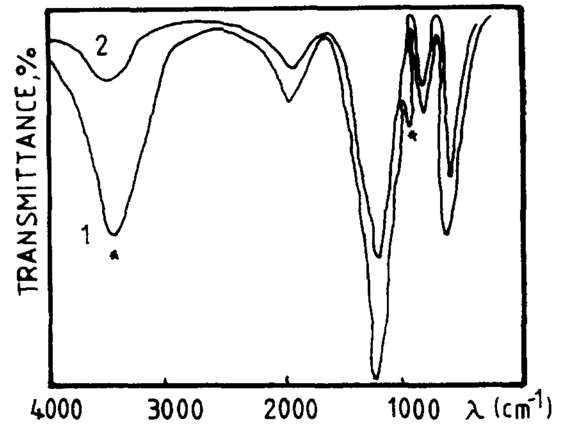

Fig. 3. IR spectra of SiO_2 (1) and RuO_2–SiO_2 (2) gels, thermally treated.

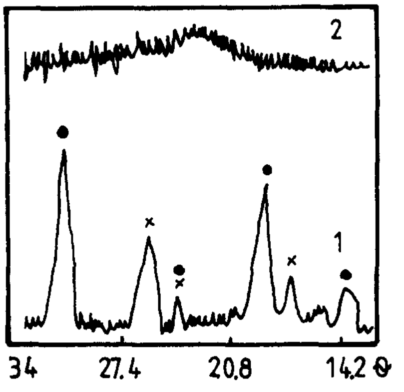

Fig. 4. X-ray diffraction patterns of RuO_2–TiO_2 (1) and RuO_2–SiO_2 (2) gels (●, rutile; X, RuO_2).

Fig. 2 shows the IR transmittance spectra of the RuO_2–TiO_2 samples. The 3420 cm^{-1} and 2960 cm^{-1} bands are attributed to the catalyst hydroxyl groups and to the OH from water and propylic alcohol which are occluded in the pores. Around 1600 cm^{-1} the OH band of the water is observed in the gel (spectrum 1).

The band of 500–600 cm^{-1} is assigned to Ti–O in amorphous TiO_2 and that of 1100 cm^{-1} is a typical C–O band that corresponds to the

Fig. 5. Scanning electron micrograph of RuO_2–TiO_2/glass microporous membrane.

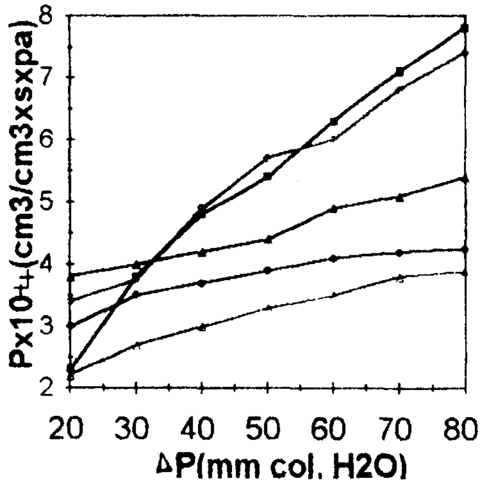

Fig. 6. Permeability as a function of the difference of pressure between the two sides of the membrane ($T = 26$°C; - - -, glass membrane; —, catalytic membrane; ○, O_2; △, C_3H_7OH; ■, RuO_2; ▲, RuO_2–TiO_2; ●, RuO_2–SiO_2).

Table 1
Effective diffusion coefficients (O_2 from air)

Membrane	$D_{ef}(cm^2/s) \times 10^8$
Glass	5.2
RuO_2/glass	5.9
RuO_2–TiO_2/glass	2.8
RuO_2–SiO_2/glass	0.84

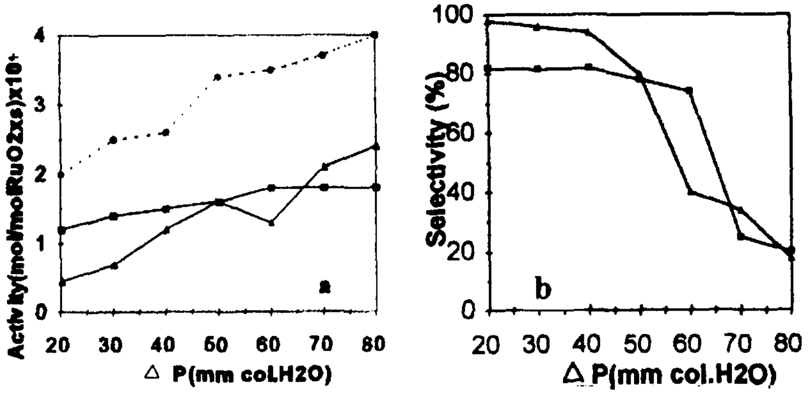

Fig. 7. Activity (a) and selectivity (b) as a function of ΔP (—, 40°C; - - -, 70°C; ■, RuO_2/glass; ▲, RuO_2–TiO_2/glass).

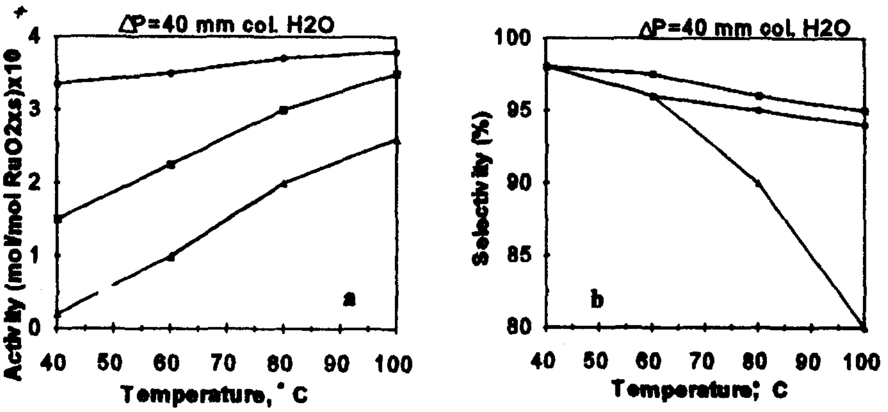

Fig. 8. Activity (a) and selectivity (b) as a function of the temperature (●, RuO_2–SiO_2/glass; ■, RuO_2/glass; ▲, RuO_2–TiO_2/glass).

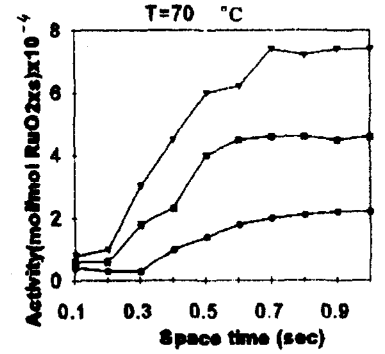

Fig. 9. Activity of RuO_2–TiO_2 membrane versus the space time ($cm^3 \times s/cm^3$) at different partial pressure of isopropylic alcohol (●, 0.2; ■, 0.5; ▼, 1.0).

unreacted alkoxide. After the thermal treatment these bands disappear.

The infrared spectra of the RuO_2–SiO_2 samples are presented in Fig. 3 (spectrum 2) and compared to SiO_2 (spectrum 1). As one can observe, the presence of RuO_2 induces a decrease in the intensity of the OH band located at 3455 cm^{-1} and a strong decrease in the intensity of the shoulder of 952 cm^{-1}. It could indicate that ruthenium coexists both on silica surface, as RuO_2 and is intercalated inside the silica network.

X-ray diffraction patterns of the samples calcined at 600°C are shown in Fig. 4. The RuO_2–SiO_2 sample shows an amorphous structure whereas the RuO_2–TiO_2 sample is very well crystallized.

SEM observations of the RuO_2–TiO_2 supported membrane show a continuous and homogeneous film of RuO_2–TiO_2 on which TiO_2 forms islands (Fig. 5). RuO_2 deposition by impregnation of the glass membrane does not generate a continuous film.

The effective diffusion coefficients (D_{ef}) and permeability of O_2 and C_3H_7OH vapour through the membranes are shown in Fig. 6 and Table 1. The values of the effective diffusion coefficients are low compared to the permeability coefficients.

After the sol–gel layer deposition D_{ef} coefficients are not significantly modified and the influence of ΔP on the permeation decreases.

Theoretically, oxidation of the isopropylic alcohol occurs to acetone, but other products of oxidation are also possible. The catalytic activity (expressed as: the ratio of the reacted alcohol moles × time^{-1}-to-RuO_2 moles) and selectivity (expressed as: acetone yield) were recorded as a function of ΔP, temperature and space time (Fig. 7, Fig. 8 and Fig. 9). The dependence of the activity and selectivity on ΔP was accounted for in terms of mass transfer processes.

Comparing the activity of the membranes one can observe the following variation: RuO_2–$TiO_2 < RuO_2 < RuO_2$–SiO_2. These differences are not due to the membrane permeabilities but to the effect of oxides coupling in the mixture. The glass membrane support is inactive in this reaction.

During the sol preparation, the titanium or silicon alkoxide forms a homogeneous mixture with ruthenium precursor. This induces the possibility to find the ruthenium partially incorporated into the titania or silica network. This process is more evident in the case of silica. RuO_2 stabilizes the superficial OH groups of silica that are included in its coordination sphere. In this way the silica mainly favours a high dispersion of the ruthenium and the activity of the RuO_2–SiO_2/glass membrane in the isopropylic alcohol oxidation is higher than in the case of RuO_2–TiO_2.

4. Conclusions

RuO_2–TiO_2 and RuO_2–SiO_2 membranes have been prepared by the sol–gel process on a microporous glass support. For comparison, a RuO_2 impregnated microporous glass support has been prepared, too. The RuO_2–TiO_2 membrane contains a mixture of oxides in which the interactions are weak. In the case of silica the ruthenium is merely incorporated in the silica network. RuO_2 stabilizes the superficial OH groups and their basicity favours its activity.

The differences in the activity of the investigated catalytic membranes are not the effect of the permeability characteristics but of the oxide coupling in the sol–gel derived materials. The possible electronic effects of TiO_2 upon the RuO_2 do not favour the isopropylic alcohol oxidation.

References

[1] J.N. Armor, Appl. Catal., 49 (1989) 1.
[2] H.P. Hsieh, Catal. Rev. Sci. Eng., 33 (1991) 1.
[3] T. Ioannides and G.R. Gavales, J. Membrane Sci., 77 (1993) 221.
[4] Y.V. Gokhale, R.D. Noble and J.L. Falconer, J. Membrane Sci., 77 (1993) 197.
[5] N. Itoh and W. Chun Xu, Appl. Catal., A Gen., 107 (1993) 83.
[6] G. Capannelli, A. Bottino, G. Gao, A. Grosso, A. Servida, G. Vitulli, A. Mastantuaono, R. Lazzaroni and P. Salvadori, Catal. Lett., 20 (1993) 287.
[7] V.M. Gryaznov, V.I. Vedernikov and S.G. Gulyanova, Kinet. Katal., 27 (1986) 129.
[8] N. Itoh, W. Chun Xu and K. Haraya, J. Membrane Sci., 66 (1992) 149.
[9] Z.D. Ziaka, R.G. Minet and T.T. Tsotsis, J. Membrane Sci., 77 (1993) 221.
[10] Y. Nigara and B. Cales, Bull. Chem. Soc. Jpn., 59 (1986) 1997.
[11] V.M. Gryaznov, V.I. Vedernikov and S.G. Gulyanova, Kinet. Katal., 27 (1986) 142.
[12] K. Omata, S. Hashimoto, H. Tominaga and K. Fujimoto, Appl. Catal., A: General, 52 (1989) L1.
[13] A. Julbe, C. Guizard, A. Larbot, L. Cot and A. Giroir-Fendler, J. Membrane Sci., 77 (1993) 137.
[14] R. Gomez, T, Lopez, S. Castillo and R.D. Gonzalez, J. Sol-Gel Sci. Technol., 1 (1994) 205.