ELSEVIER

Catalysis Today 82 (2003) 91–98

CATALYSIS TODAY

www.elsevier.com/locate/cattod

AgBiVMo oxide catalytic membrane for selective oxidation of propane to acrolein

Baichun Zhu, Hongbo Li, Weishen Yang*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
P.O. Box 110, Dalian 116023, PR China

Abstract

A metal ions (Ag, Bi, V, Mo) modified sol–gel method was used to prepare a mesoporous $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalytic membrane which was used in the selective oxidation of propane to acrolein. By optimizing the preparation parameters, a thin and perfect catalytically active membrane was successfully prepared. SEM results showed that the membrane thickness is ~5 μm. XRD results revealed that $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ with a Scheelite structure, which is catalytically active for the selective oxidation of propane to acrolein, was formed in the catalytic membrane only when AgBiVMoO concentrations were higher than 40%. Catalytic reaction results demonstrated that the selective oxidation of propane could be controlled to a certain degree, such as to acrolein, in the catalytic membrane reactor (CMR) compared to the fixed bed reactor (FBR). For example, a selectivity of 54.85% for acrolein in the liquid phase was obtained in the CMR, while only 8.31% was achieved in the FBR.

Keywords: Oxidation; Propane; Acrolein; Membrane reactor

1. Introduction

Acrolein usually is used as an intermediate to produce acrylic acid, which is an important industrial chemical with an annual world capacity of 6 billion pounds in 1997 [1]. The industrial process for production of acrolein is the catalytic selective oxidation of propylene. Compared to propylene, propane is a cheaper, readily available raw material, so direct catalytic selective oxidation of propane would be a very attractive route for the production of acrolein. However, the challenge for the process is how to achieve a high selectivity for the desired product, because the intermediates, i.e. olefins, as well as desired product, i.e. acrolein, are usually more reactive than the raw material, i.e. propane, and easier to be deeply oxidized to CO_x and H_2O.

In order to achieve high selectivity to acrolein for the selective oxidation of propane, researchers have devoted a lot of work to screening different kinds of catalysts to find one with high selectivity [1–13]. Among these catalysts, $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ is a good one for the selective oxidation of propane to acrolein. However, the yield of the desired product during the selective oxidation of propane to acrolein does not exceed 10% per pass as up to now [1,2]. To control the selectivity, researchers have attempted to combine different catalysts, such as a catalyst for oxidative dehydrogenation of propane to propylene and a catalyst for selective oxidation of propylene to acrolein, in one reactor [2] in which 11.3% yield of acrolein was achieved with 62.8% acrolein selectivity. On the other hand, some new concepts were also

---

* Corresponding author.
E-mail address: yangws@dicp.ac.cn (W. Yang).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00206-2

developed to control the selectivity for the selective oxidation of propane to acrolein, by using a membrane reactor, in which the membrane was used as reactant distributor to introduce a reactant (O_2 or propane) in a controllable manner, which could regulate the reaction to the better selectivity [14,15]. Or the membrane was used as products (acrolein and H_2O) separator to remove the products from the reaction system simultaneously, therefore, the product was not allowed to be further oxidized to CO_x and H_2O [16]. In the former case, we tried four different flow arrangements of propane and O_2 in a tubular membrane reactor packed with $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalyst. The highest selectivity of 18% was obtained for dosing propane from the shell side to the tube side and feeding O_2 in the tube side [15]. In the latter case, Kolsch et al. [16,17] used an oxygenates-selective silica modified mesoporous membrane to simultaneously remove acrolein and H_2O from the membrane reactor in the process of reaction, the selectivity of acrolein could be increased by a factor of 2–3 compared with co-feed packed bed reactor at similar propane conversion.

For both cases of membrane reactors mentioned above, the membranes are inert and are only used to add reactant to (or remove products from) reaction system. The membrane itself does not work as a catalyst for the reaction. This kind of membrane reactor is called inert membrane reactor (IMR). There is another kind of membrane reactor, called catalytic membrane reactor (CMR), in which the membrane itself has an intrinsic catalytic activity for the reaction. In CMR, one of operation mode is that the reactants permeate through the membrane in the Knudsen regime and are introduced in a flow-through mode [14]. The idea to improve catalytic selectivity for the selective oxidation of propane to acrolein in CMR is based on the fact that the catalytic layer of the membrane is very thin (5–10 μm), which can greatly reduce the contact time between aimed product and catalytic layer to prevent the aimed product be further oxidized to CO_x and H_2O. At same time, the catalytic layer is mesoporous, and continuously and compactly arranged, which guarantees that the membrane has a relative high contact surface and reactants have a good contact with the catalyst.

In this paper, we will use a sol–gel technique to prepare a catalytically active membrane and apply such membrane to the process of selective oxidation of propane to acrolein.

2. Experimental

2.1. Preparation of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalyst by complex method

For comparison, we prepared $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalysts by complex method. First we prepare metal ions complex solution, then dry the solution and calcine the catalyst at certain temperation. The typical procedure for the preparation of metal ions (Ag, Bi, V, Mo) complex solution was prepared as following. Twenty-eight grams EDTA acid was added in 60 ml ammonia water (50%, v/v) to get a transparent solution, slowly adding 41.23 g $Bi(NO_3)_3{\cdot}5H_2O$ (A.R.) in the solution until all Bi salt dissolved, then adding 0.17 g $AgNO_3$ to get solution (a). Fifteen grams EDTA acid was added in 60 ml ammonia water (50%, v/v) to get a transparent solution, then adding 4.9 g V_2O_5 (A.R.), then heating and stirring until V_2O_5 dissolved completely to get solution (b). 7.94 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (A.R.) was added in 50 ml distilled water to make all the chemical dissolved completely, then adding 13 g EDTA acid (A.R.). If EDTA acid precipitated, adding some of ammonia water (50%, v/v) to get a transparent solution (c). Solutions (a), (b), (c) are mixed and stirred to get 0.1 mol $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ complex solution. The concentration of complex solution is 3.64×10^{-4} mol/ml. The resulted product was calcined at 380 °C for 6 h, 600 °C for 6 h separately.

2.2. Preparation of catalytically active membrane

The mesoporous catalytically active membrane was prepared by modified sol–gel method, as shown Fig. 1.

For preparation of catalytically active membrane by modified sol–gel method, we started with the preparation of γ-AlOOH sol, then modified the γ-AlOOH sol with metal ion complexes (Ag, Bi, V, Mo) possessing catalytic function for selective oxidation of propane to acrolein. After getting the modified γ-AlOOH sol, the dip-coating method was used to deposit the modified γ-AlOOH sol onto the porous α-Al_2O_3 support of

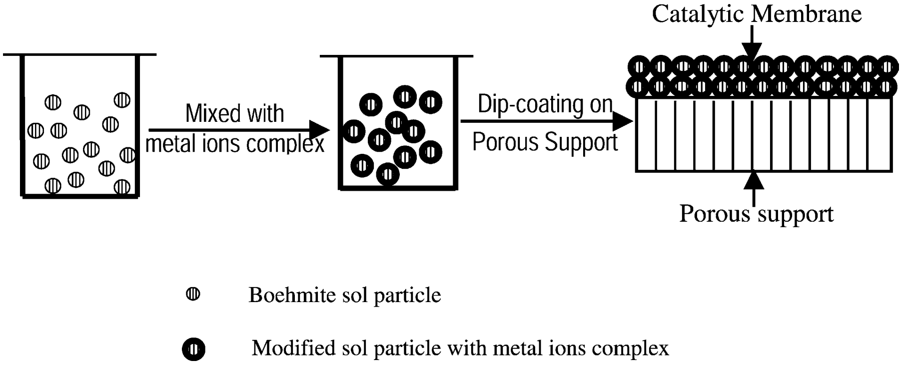

Fig. 1. Schematic representation for preparation of catalytically active membrane by modified sol–gel method.

~0.6 μm average pore size and ~40% porosity, then calcined with great care to get a catalytic membrane.

Preparation of γ-Al_2O_3 sol. PURAL SB power (Dispersal 55909, Corporation, Germany) was used as the starting material which is a kind of industrial product with boehmite structure (γ-AlOOH). The detailed preparation process is illustrated in Fig. 2. Firstly, the SB powder was mixed with de-ionized water, and the suspension in a certain concentration was obtained, then the suspension was heated at 80 °C and refluxed for 30 min in order to hydrate the boehmite particulates sufficiently, then some nitric acid was added to peptize the boehmite particles to form the γ-AlOOH sol, and the sol was aged for 5 h at 80 °C under refluxing.

Preparation of metal ions (Ag, Bi, V, Mo) complex solution. The typical procedure for the preparation of metal ions (Ag, Bi, V, Mo) complex solution was described in detail in experimental Section 2.1. The concentration of complex solution used here is 3.64×10^{-4} mol/ml.

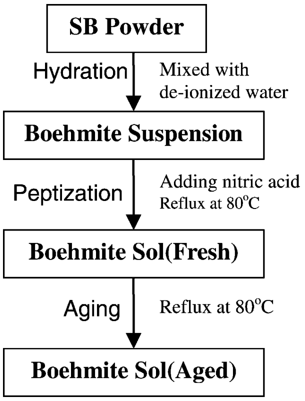

Fig. 2. Preparation process for particulate boehmite sol from SB powder.

Modification of γ-Al_2O_3 sol by metal ions (Ag, Bi, V, Mo) complex. The metal ions (Ag, Bi, V, Mo) complex solution was added to the aged γ-AlOOH Sol. After stirring for 2 h with strict control of the pH value of 3–4, the metal ions (Ag, Bi, V, Mo) modified sol was obtained.

Dip-coating of modified sol on the porous α-Al_2O_3 support. Before dip-coating, the porous α-Al_2O_3 tube was polished with fine sand paper and cleaned with microwave for several minutes, then dried and calcined at 550 °C. To ensure the valid membrane length was 6 cm, both end part of the tube were sealed with glaze. α-Al_2O_3 tube was dipped into the modified sol for several seconds at room temperature till a gel layer was formed, then take it out and put it in a dust-free box for drying overnight. The supported catalytic membrane was calcined at 600 °C with temperature raising rate of 0.3 °C/min for 6 h. The above dipping and calcination procedures were repeated for several times until a weight increase around 50 mg was obtained.

2.3. Characterization of the catalytically active membrane

The particle distributions of the γ-AlOOH sol (1 mol/l) with different nitric acid concentrations were measured by the quasi-elastic laser light scattering method (N4 Plus Particle Sizer, COULTER, USA).

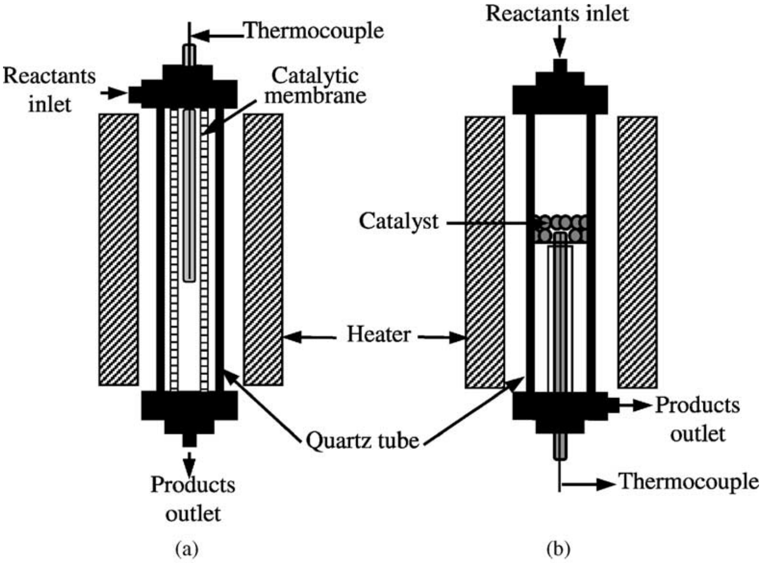

Fig. 3. The configurations of CMR (a) and FBR (b).

The pore size distribution and specific surface area of the catalytically active membrane were obtained from the nitrogen adsorption and desorption isotherm at 77 K using BET surface analyzer (Coulter 100 CX, USA).

The phase structure of the catalytically active membrane was determined by X-ray powder diffractometry (Rigaku D/Max-RB) with Cu $K\alpha_I$ radiation at 40 kV × 100 mA with continuous scanning rate of 3°/min from 5° to 80°.

The morphology of the catalytically active membrane was observed by a scanning electron microscopy (SEM, JEM-5600LV). Different magnifications were applied depending on the purposes.

2.4. Catalytic reaction

Catalytic reaction in CMR. The catalytic reaction in CMR was carried out at atmospheric pressure, as shown in Fig. 3a. The reactants of C_3H_8, O_2 and N_2 were introduced in the shell side of CMR, then pass through the catalytically active membrane to the tube side of CMR, from which the products and un-reacted reactants came out to a cooling trap for collecting the liquid products. The reaction conditions were as following. The catalyst loading was 50–100 mg, the reaction temperature was 400 °C, the feed gas molar ratio of propane/O_2/N_2 is 37/53/10, the total flow rate is 100 ml/min.

Catalytic reaction in fixed bed reactor (*FBR*). The catalytic reaction in FBR was carried out at atmospheric pressure, as shown in Fig. 3b. The reactants of C_3H_8, O_2 and N_2 were introduced into FBR, then the products and un-reacted reactants came out to a cooling trap for collecting the liquid products. The reaction conditions were as following. The catalyst loading was 2 g (diluted with 10 g quartz), the reaction temperature was 400 °C, the feed gas molar ratio of propane/O_2/N_2 is 37/53/10, the total flow rate is 100 ml/min.

The liquid products were analyzed by a gas chromatograph (Hewlett Packard 6890) equipped with a capillary column by using FID and propanol as inner standard. The selectivity of each liquid product was defined as the fraction of all liquid products in the liquid phase.

3. Results and discussion

3.1. Preparation of catalytically active membrane

As described in Section 2.2, the catalytically active membrane was prepared by modified sol–gel method. First, we prepared a stable γ-AlOOH sol

Table 1
Effect of nitric acid concentration on the properties of γ-AlOOH sol (1 m) prepared from SB powder

Samples	$[HNO_3]$ in sol (M)	pH	Viscosity (MPa s)	Particle diameter (nm) (≥90% by mass)	Stability
DAL-06	0.06	3.46	1.2	30–75	Sol with less precipitate (partially peptized)
DAL-08	0.08	3.40	1.4	19–60	Stable sol
DAL-09	0.09	3.37	1.3	38–75	Stable sol
DAL-10	0.1	3.37	1.35	30–60, 95–120	Double peaks, relatively stable sol
DAL-12	0.12	3.13	1.65	60–150	Unstable sol (8–9 days, gel)

with small particle size and narrow size distribution. As shown in Fig. 2, nitric acid is used to peptize the suspension to avoid introducing anion impurities for the preparation of γ-Al_2O_3 sol. It has been known that the acid concentration has an effect on the pH value, the viscosity and the particle diameter of the sol, so we change the concentration of the nitric acid in the solution by changing the quantities of nitric acid used in the peptizing step. In the all experiments, the concentration of the γ-AlOOH sol was maintained at 1 mol/l. Typical results are listed in Table 1.

The viscosity of the colloid is one kind of expression for the viscoelasticity, which is mainly controlled by the degree of the aggregation and disaggregation of the colloid particles. It can be seen from Table 1 that the colloid has the lowest viscosity when the acid concentration is 0.06 M, which means that boehmite partial peptization occurred with less precipitate in the sol. The viscosity of the sol almost remains constant when the acid concentration is increased to 0.08–0.1 M, which means that a stable sol without precipitate is obtained. Further increase of the acid concentration, such as to 0.12 M, will result in easier gel formation within a short time, such as 8–9 days, and the viscosity of the sol reaches at the maximum in this case.

The particle distributions of the γ-AlOOH sol (1 mol/l) with different nitric acid concentrations were measured by the quasi-elastic laser light scattering method (N4 Plus Particle Sizer, COULTER), as shown in Fig. 4. It can be seen that the sol with the smallest average diameter and a narrow size distribution is obtained when the nitric acid concentration is 0.08 M. With the increase of the acid concentration, the particle size of the γ-AlOOH sol turns to be bigger and its distribution becomes wider. Further increasing the acid concentration, such as 0.12 M, causes the γ-AlOOH sol particles grow and aggregate intensively.

It can be concluded that the optimum concentration of nitric acid for getting a small sol particles with narrow particle size distribution is 0.08 M. We modified the γ-AlOOH sol with metal ions (Ag, Bi, V, Mo) solution, as described in the experimental Section 2.1, to get the metal ions modified sol. The typical properties of the metal ions modified γ-AlOOH sol with different $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ concentrations are listed in Table 2.

Table 2 shows that the viscosity of the metal ions modified γ-AlOOH sol increases with the increase of AgBiVMoO concentrations, and the particle size increases sharply at the beginning, then increases gradually because addition of metal ions may destroy

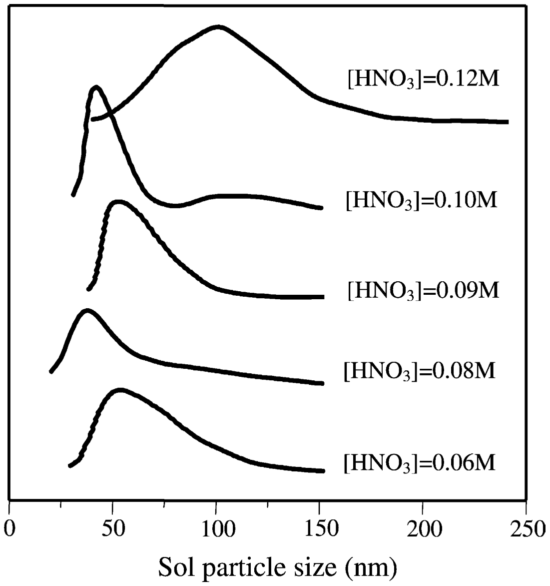

Fig. 4. Particle size distribution of boehmite sol with different acid concentrations prepared from SB powder.

Table 2
Effect of AgBiVMoO concentrations on properties of the modified sol

AgBiVMoO concentration (wt.%)	Viscosity (MPa s)	Particle diameter (nm)	wt.% (by mass)
80	2.3	2383, 3000	6, 91
60	2.0	598, 3000	16, 83
40	1.9	948, 1194	5.2, 94.8
20	1.9	598, 753	37.6, 55.3
10	1.29	598, 753	64.7, 35.3

Table 3
Effect of AgBiVMoO concentrations on pore structure of mesoporous AgBiVMoO catalytic membrane

AgBiVMoO concentration (wt.%)	BET area (m^2/g)	Pore radius (nm)	Specific pore volume (cm^3/g)	Porosity[a] (%)
40	89.25	1–10	0.311	52.43
20	159.54	1–10	0.4143	57.48
10	196.50	1–10	0.4863	64.77
0	230	1–10	0.4984	64.84

[a] Porosity is calculated based on the formula: $\theta = V_p/(V_p + 1/\rho_t)$, where θ is the porosity, V_p the specific pore volume, ρ_t the true density of alumina ($\rho_t = 3.7\,g/cm^3$).

the stableness of the γ-AlOOH sol, and make the sol particles to aggregate at the beginning. The different particle sizes of the γ-AlOOH sol modified with different AgBiVMoO concentrations result in different pore size and surface area of the catalytic membrane as shown in Table 3.

It can be seen from Table 3 that with the increasing of AgBiVMoO concentration, BET surface area decreases gradually at the beginning, then decreases sharply when the AgBiVMoO concentration reaches at 40 wt.%, which shows a good agreement with the changes of metal ions modified γ-AlOOH sol particles. Besides the pore size and BET surface area, we also identified the phase structure of the AgBiVMoO catalytic membrane, as shown in Fig. 5.

Fig. 5 shows that XRD patterns of the AgBiVMoO catalytic membrane are identical to that of γ-AlOOH when the concentration of AgBiVMoO is lower than 40%. However, the typical scheelite structure of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalyst, which is the active phase for the selective oxidation of propane to acrolein, appears when the concentrations of AgBiVMoO are higher than 40%. So only the catalytically active membranes with 40 and 80% AgBiVMoO concentrations were chosen for the catalytic evaluations in the membrane reactor.

Fig. 6 shows the SEM photos taken from the cross view and top view of the catalytically active membrane on the porous α-Al_2O_3 support with AgBiVMoO concentration of 40%. It can be seen that the thickness of catalytically active membrane is around 5 μm (Fig. 6a), and there is no crack or pinhole on the surface of the membrane (Fig. 6b). In addition, there indeed are a lot of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ catalyst particles (less than 1 μm) in the membrane. The

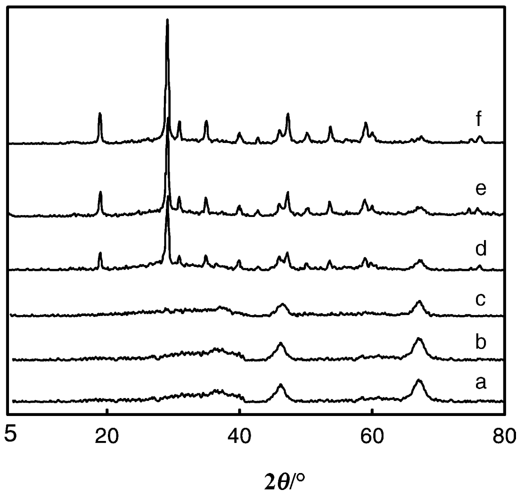

Fig. 5. XRD patterns of: (a) γ-AlOOH; (b) γ-AlOOH modified by 10% AgBiVMoO; (c) γ-AlOOH modified by 20% AgBiVMoO; (d) γ-AlOOH modified by 40% AgBiVMoO; (e) γ-AlOOH modified by 60% AgBiVMoO; (f) γ-AlOOH modified by 80% AgBiVMoO.

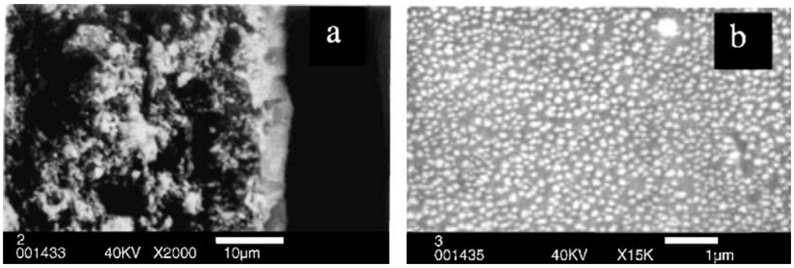

Fig. 6. SEM photos of catalytic membrane prepared by modified sol–gel method: (a) cross view; (b) top view.

Table 4
Comparison of selectivities of liquid products in different reactors

	Selectivities in liquid phase (%)					
	Acrolein	Acrylic acid	Acetic acid	Methanol	Acetone	Formaldehyde
FBR	8.31	11.15	23.65	43.50	4.25	9.14
Membrane reactor (40%)	54.85	trace	trace	17.21	11.17	16.77
Membrane reactor (80%)	38.26	trace	trace	14.71	18.84	28.18

pore radius of the catalytically membrane is less than 10 nm (Table 3).

3.2. Selective oxidation of propane to acrolein in CMR

Table 4 lists the selectivity of acrolein in the liquid phase for the selective oxidation of propane to acrolein in CMR and FBR. It can be seen that most of acrolein was further oxidized to acrylic acid (11.15% selectivity in the liquid phase) and acetic acid (23.65% selectivity in the liquid phase) in FBR while there were only a trace amount of further oxidation products, such as acrylic acid and acetic acid, were formed in CMR. So, as high as 54.85% selectivity to acrolein in the liquid phase was obtained in CMR, while only 8.31% selectivity to acrolein in the liquid phase was achieved in FBR. These results demonstrate that the selectivity to acrolein for the selective oxidation of propane can be controlled to a high level by using CMR.

4. Conclusions

A crack-free catalytically active membrane with pore radius of less than 10 nm was successfully prepared by the modified sol–gel technique. By controlling the concentrations of AgBiVMoO, the catalytic active phase, i.e. $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ with scheelite structure, was formed on the membrane surface and in the γ-Al_2O_3 membrane matrix. The results for the selective oxidation of propane to acrolein in the catalytically active membrane reactor demonstrated that the contact time between aimed product and catalytic layer can be greatly reduced by the reducing the catalytic layer to a few micrometer, such as 5 μm. As a result, the aimed product, such as acrolein, was prevented to be further oxidized to acrylic acid and CO_x and H_2O.

Acknowledgements

The authors gratefully acknowledge financial supports from the Ministry of Science and Technology of China (Grant No. G1999022401) and the National Natural Science of Foundation of China (Grant No. 59789201).

References

[1] M.M. Lin, Appl. Catal. A 207 (2001) 1.
[2] M.Yu. Sinev, O.V. Udalova, Y.P. Tulenin, L.Ya. Margolis, V.P. Vislovskii, R.X. Valenzuela, V.C. Corberan, Catal. Lett. 69 (2000) 203.

[3] J. Barrault, C. Batiot, L. Magaud, M. Ganne, in: Proceedings of the Third World Congress on Oxidation Catalysis, vol. 110, 1997, p. 375.

[4] D.L. Stern, R.K. Grasselli, J. Catal. 167 (1997) 550.

[5] A. Kaddouri, C. Mazzocchia, E. Tempesti, Appl. Catal. A 180 (1999) 271.

[6] W. Ueda, K. Oshihara, Appl. Catal. A 200 (2000) 135.

[7] P. Botella, B. Solsona, A. Martinezarias, J.M.L. Nieto, Catal. Lett. 74 (2001) 149.

[8] L. Luo, J.A. Labinger, M.E. Davis, J. Catal. 200 (2001) 222.

[9] K. Oshihara, T. Hisano, W. Ueda, Top. Catal. 15 (2001) 153.

[10] Y.C. Kim, W. Ueda, Y. Moro-Oka, J. Chem. Soc., Chem. Commun. 10 (1989) 652.

[11] M. Baerns, O.V. Buyevskaya, M. Kubik, O. Ovsitser, O. Seel, Catal. Today 33 (1997) 85.

[12] H.Z. Du, X.G. Wang, Y.W. Chi, Shiyou Huagong 26 (1997) 1.

[13] X.G. Wang, H.Z. Du, Y.W. Chi, Shiyou Huagong 26 (1997) 73.

[14] W.S. Yang, G.X. Xiong, Curr. Opin. Solid State Mater. Sci. 4 (1999) 103.

[15] W.S. Yang, P. Yang, W.L. Fang, L.W. Lin, Stud. Surf. Sci. Catal. 130 (2000) 2705.

[16] P. Kolsch, M. Noack, R. Schafer, G. Georgi, R. Omorjan, J. Caro, J. Membr. Sci. 198 (2002) 119.

[17] P. Kolsch, Q. Smejkal, M. Noack, R. Schafer, J. Caro, Catal. Commun. 3 (2002) 465.