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Small-scale hydrogen production from propane

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Abstract

Partial oxidation and oxidative steam reforming of propane were investigated over 0.01 wt.% Rh/Al_2O_3 foam catalysts. High selectivity to hydrogen was obtained for both reactions, but addition of steam to the reactant mixture gave higher selectivity to hydrogen. Stability tests over 7 h revealed that the catalytic activity of Rh was quite stable under partial oxidation conditions. Higher loss in Rh activity was observed when steam was present in the reactant mixture. FE-SEM images showed that Rh particle size and distribution are modified under partial oxidation and oxidative steam reforming conditions. However, these changes were more distinct on the catalyst used for oxidative steam reforming.

Keywords: Propane; Hydrogen; Partial oxidation; Oxidative steam reforming; Rh catalyst; FE-SEM

1. Introduction

Hydrogen is important in oil refineries and the chemical industry, and it is becoming attractive as a clean fuel for combustion processes and fuel cells. Conversion of lower alkanes by catalytic partial oxidation at short contact times is one promising route for hydrogen or synthesis gas production.

The short contact time regime obtained using various structured catalysts [1–4] is particularly suitable for fast oxidation reactions [5–8]. Several studies devoted to oxidation reactions of light hydrocarbons concluded that Rh is one of the most suitable catalysts for the production of hydrogen [9–11], especially if performed in a short contact time regime [12–16].

An essential property required for catalytic systems for production of hydrogen is stability under oxidising conditions. It has been reported that Rh-coated α-Al_2O_3 foam catalyst did not show activity loss at 1000 °C over several hours [12]. The stability and selectivity to hydrogen of reducible- and irreducible-oxide supported rhodium catalysts was investigated for partial oxidation of methane by Ruckenstein and Wang [17]. It was concluded that irreducible-oxides (MgO, γ-Al_2O_3, SiO_2, Y_2O_3, La_2O_3) are suitable supports with high stability due to strong interactions with the rhodium. The strong metal–support interaction between rhodium and alumina support, inhibiting sintering and growth of large of rhodium oxide particles below 900 °C, was also reported by Beck et al. [18]. Rh/Al_2O_3 was found to have the highest stability of all tested catalysts (Rh, Ru, Pd, Pt, Ni, Co supported on Al_2O_3) for hydrogen production by steam reforming of 2-propanol at 400 and 500 °C [19].

In our work, Rh-impregnated alumina foams have been tested for catalytic partial oxidation and oxidative steam reforming of propane as potential high-throughput structured catalysts. The main subject of this paper is the stability of the Rh foam catalyst. Furthermore, the structural details of the catalysts and possible changes under the conditions applied have been investigated using field emission scanning electron microscopy (FE-SEM). Finally, we wish to establish to which degree any structural changes can be directly linked to changes in activity and selectivity.

2. Experimental

Rh structured catalysts were prepared by impregnation of extruded alumina foams of 84% porosity (Goodfellow) with

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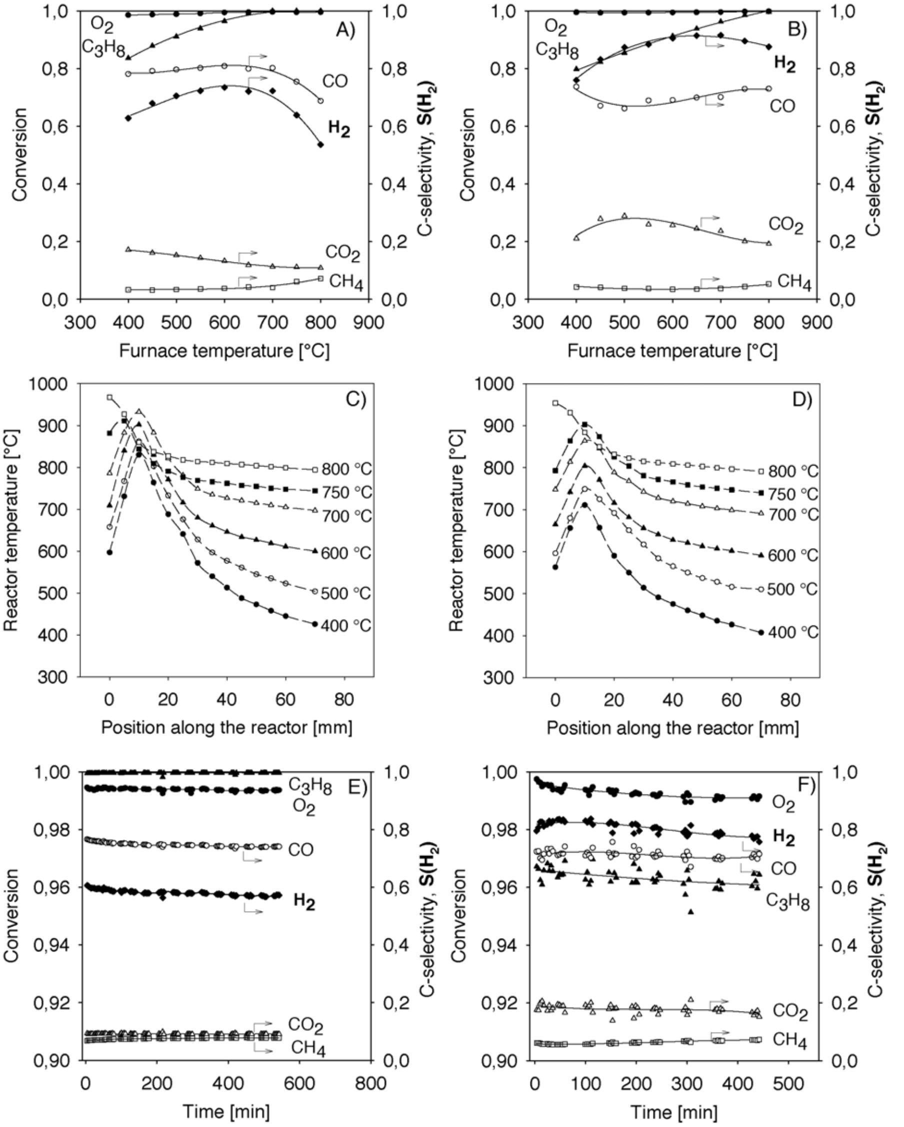

Fig. 1. Results of reaction experiments for POX (A, C and E) and OSR (B, D and F) over 0.01 wt.% Rh/Al_2O_3. (A and B) Conversion, C-selectivity and selectivity to H_2 as a function of furnace temperature. (C and D) Temperature profiles along the reactor for different furnace temperatures. Position 0 corresponds to the inlet of the foam catalyst. (E and F) Conversion, C-selectivity and selectivity to H_2 as a function of time-on-stream at 700 °C furnace temperature. Total flow rate: 1000 Nml/min. (A, C and E) POX feed flows (Nml/min): C_3H_8 (101), O_2 (190), and N_2 (709). (B, D and F) OSR feed flows (Nml/min): C_3H_8 (100), O_2 (150), N_2 (450), and H_2O (300).

99.5% nominal purity. Cylindrical foam pieces (3 mm i.d., 15 mm o.d., 12.7 mm length) were cut and then impregnated in $Rh(NO_3)_3 \cdot 2H_2O$ solution to obtain a final Rh loading of 0.01wt.%, as estimated by the solution uptake. The impregnated foams were dried at 100 °C for 1 h and calcined in flowing air at 600 °C for 4 h. Reduction was performed in situ at 700 °C for 1 h in a flow of hydrogen prior to the reaction experiment. A short contact time reactor set-up was arranged by placing the Rh-impregnated catalyst between two inert cordierite (400 cells/in.^{2}) pieces (3 mm i.d., 15 mm o.d., 7 mm length) in a quartz reactor.

Experiments were carried out in a continuous reactant flow at close to atmospheric pressure and furnace temperatures in the range 300–800 °C. The temperature inside the reactor was measured by a movable thermocouple placed into a quartz tube. The reactant gas mixture consisted of propane, air and nitrogen in the case of partial oxidation (POX), with a C/O ratio equal to 0.8 [20]. For oxidative steam reforming (OSR), steam was added to the reactant mixture with C/O and H_2O/O_2 ratios of 0.5 and 2.0, respectively. The concentration of propane in the feed and the total flow rate were the same for both POX and OSR.

Each catalyst sample was subjected to the same sequence of experiments for both reaction types. Temperature-dependent experiments were performed first, followed by stability tests at 700 °C for 7 h without any treatment of the catalysts between the experiments. The Rh foam catalyst

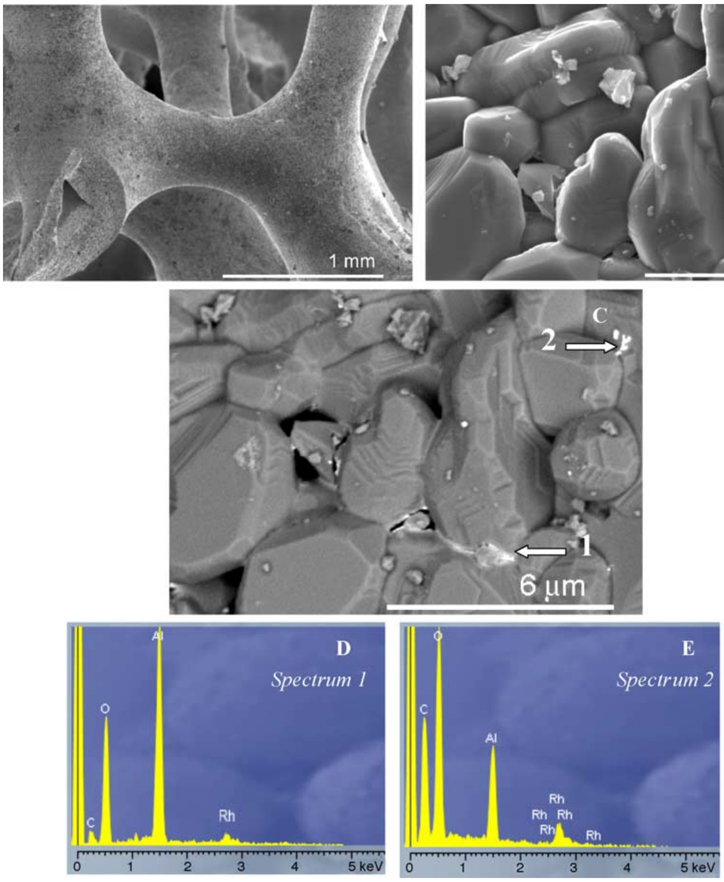

Fig. 2. FE-SEM images of 0.01wt.% Rh/Al_2O_3 foam. (A and B) Secondary electron microscopy, (C) backscattered electron microscopy, (D and E) EDS analysis from positions indicated in (C).

was then oxidised at 700 °C for 1 h in flowing air and reduced at 600 °C for 1 h in hydrogen before a second stability test was made. Then, another oxidation–reduction procedure was carried out before effects of residence time and reaction pressure were studied at 700 °C. Finally, the Rh foam catalyst was removed and characterised.

The hydrogen selectivity was calculated in order to quantify hydrogen formation relative to propane conversion, irrespective of steam content in the reactant mixture by the following Eq. (1):

$$S(H_2) = \frac{F_{\text{tot,out}}}{F_{\text{tot,in}}} \times \frac{C_{H_2,\text{out}}}{4 \times C_{C_3H_8,\text{in}} \times X_{C_3H_8}} \qquad (1)$$

where $F_{\text{tot,in}}$ and $F_{\text{tot,out}}$ are total volumetric gas flows at reactor inlet and outlet, respectively, expressed in Nml/min (0 °C, 1 bar), $C_{H_2,\text{out}}$ is the concentration of hydrogen in the outlet gas, $C_{C_3H_8,\text{in}}$ is the concentration of propane in the feed gas and $X_{C_3H_8}$ is the conversion of propane. The residence time was calculated as the ratio of void volume of Al_2O_3 foam to the total volumetric gas flow at reactor inlet [20]. A total flow rate of 1000 Nml/min then corresponds to 0.105 s residence time.

FE-SEM (Hitachi S-4300SE) was used to characterise the Rh-impregnated alumina foams before and after reaction. The 0.01wt.% Rh/Al_2O_3 foam catalysts had to be lightly coated by carbon to avoid charging. The samples were mounted so that the pore structure facing the reactants was imaged. Secondary and backscattered electron images, whose contrast is mainly sensitive to topography and composition, respectively, were recorded. The chemical composition of representative surface particles was analysed by energy dispersive spectroscopy (EDS). The unused Rh/Al_2O_3 foam sample analysed by FE-SEM was calcined but not reduced. The used catalysts had been subjected to a set of either POX or OSR experiments as described above.

3. Results and discussion

Conversion of reactants and selectivity to main products during partial oxidation (POX) and oxidative steam reforming (OSR) of propane over the Rh/Al_2O_3 foam catalyst are shown in Fig. 1A and B, respectively, as a function of furnace temperature. Aspects of temperature, residence time, pressure and contributions from homogeneous reactions are discussed elsewhere [20], but some main conclusions are summarised below. Oxygen and propane conversion increased with temperature, and was complete at 700 °C furnace temperature for POX (Fig. 1A). For OSR (Fig. 1B), oxygen conversion was complete from a

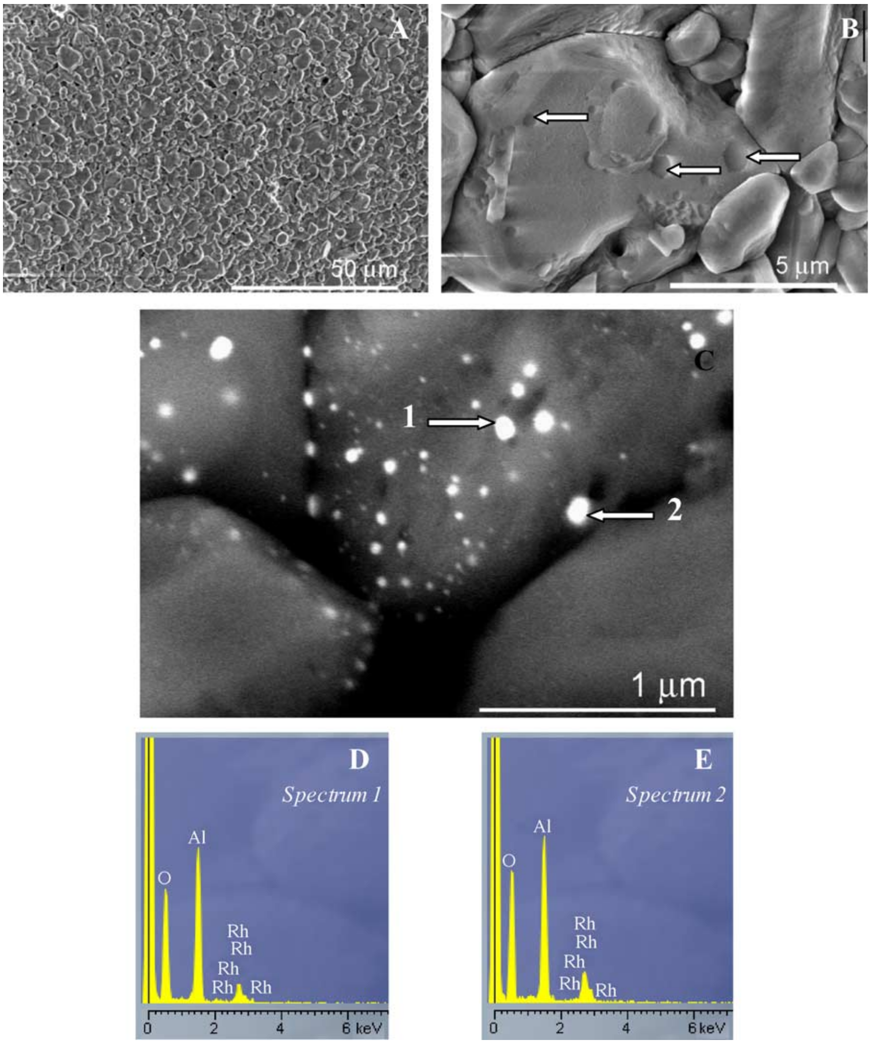

Fig. 3. FE-SEM images of 0.01wt.% Rh/Al_2O_3 foam used for POX experiments. (A and B) Secondary electron microscopy, (C) backscattered electron microscopy, (D and E) EDS analysis from positions indicated in (C). The arrow markers in (B) point to round-shaped features (pits or mounds) present on the alumina surface after reaction.

furnace temperature of 400 °C, while complete propane conversion was not obtained until 800 °C.

POX as well as OSR over the Rh/Al_2O_3 foam catalyst gave high selectivity to hydrogen and carbon monoxide (Fig. 1A and B). However, the addition of steam clearly had a positive effect on the selectivity to hydrogen, which is also predicted from our thermodynamic calculations that are not reproduced here. The selectivity to hydrogen was the highest (0.72 for POX and 0.92 for OSR) at 700 °C and decreased above this temperature for both reaction types. Therefore, 700 °C was chosen as the optimal temperature for the production of hydrogen in our system. Major side products observed during POX and OSR were carbon dioxide and methane (Fig. 1A and B). The selectivity to methane slightly increased with temperature, while the selectivity to carbon dioxide decreased above 500 °C furnace temperature. Addition of steam induced higher production of carbon dioxide and somewhat lower production of carbon monoxide. Alkenes, alkynes and higher hydrocarbons were formed in small amounts during POX and OSR as well. The combined selectivity of these hydrocarbons was 4.5% for POX and 2.5% for OSR at 700 °C furnace temperature.

Temperature profiles along the reactor axis were measured inside the cordierte pieces and Rh-impregnated foams during reaction (Fig. 1C and D). The maximum reactor temperature was significantly higher than the furnace temperature. Temperature differences of 430 and 345 °C were observed at 400 °C furnace temperature during POX and OSR, respectively. These differences decreased with temperature and, at the highest furnace temperature (800 °C), the maximum reactor temperature was 967 °C for POX and 954 °C for OSR. The temperature profiles have been discussed in detail elsewhere [20].

Fig. 1E and F displays the result of time-on-stream experiments over Rh/Al_2O_3 foam catalysts at 700 °C furnace temperature for POX and OSR, respectively. The conversion of oxygen and propane was stable over 7 h during POX, while the selectivity to hydrogen and carbon monoxide

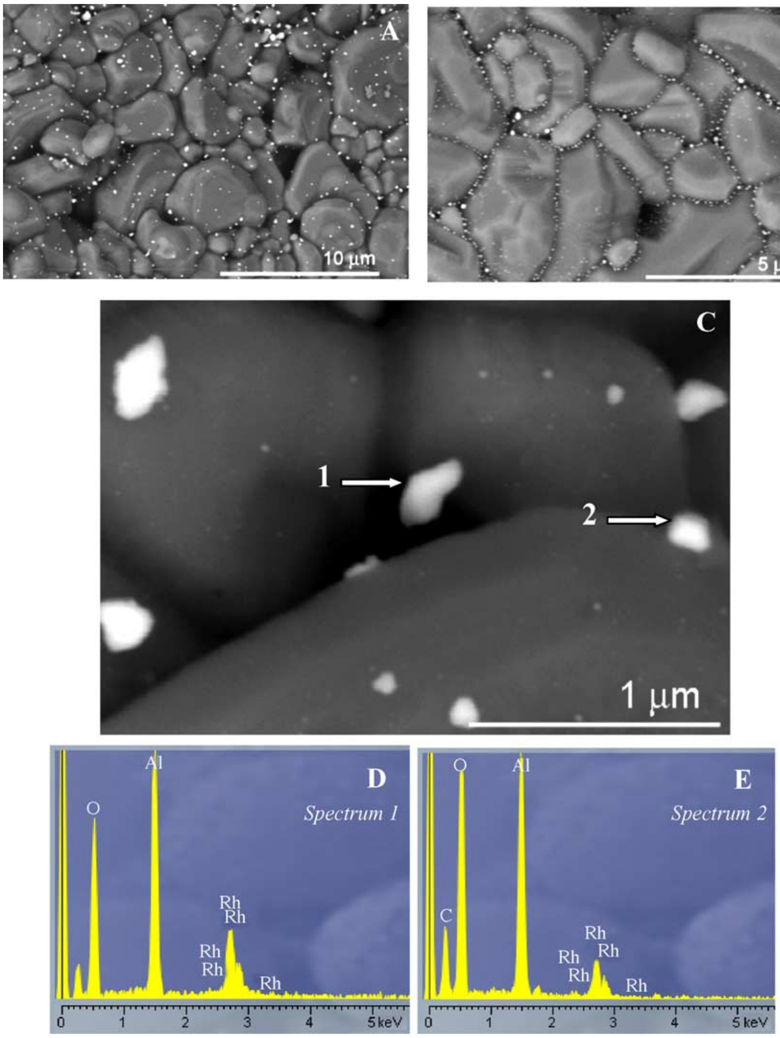

Fig. 4. FE-SEM images of 0.01 wt.% Rh/Al_2O_3 foam used for OSR experiments. (A–C) Backscattered electron microscopy, (D and E) EDS analysis from positions indicated in (C).

decreased slightly (Fig. 1E). Higher loss in catalytic activity was observed when steam was present in the reactant mixture (OSR). The conversion of oxygen and propane as well as selectivity to hydrogen and carbon monoxide gradually decreased through the 7 h period (Fig. 1F).

FE-SEM analysis results of a 0.01 wt.% Rh/Al_2O_3 foam as prepared and calcined are shown in Fig. 2. Fig. 2A displays the alumina foam macrostructure with interconnected, irregular macropores. A triangle-shaped cavity is also revealed, and these could be seen where the alumina foam structure was cut. The structure of the alumina is shown in more detail in Fig. 2B. It consists of many alumina crystallites of irregular shape and size. The diameter of the crystallites was measured to be from 0.6 to 11.3 µm. EDS analysis revealed zirconia to be present on the surface as individual particles of around 10 µm in diameter, however in very small amounts. The zirconia was also observed on non-impregnated foams, and is thus an impurity component probably introduced during manufacture. Reaction experiments over unimpregnated alumina foams were performed and the main products could be ascribed to homogeneous reactions [20]. However, a minor contribution of zirconia to the catalytic activity cannot be excluded.

Several back-scattered SEM images show Rh to be present in larger amounts on the grain boundaries between alumina particles than on the individual particle surfaces. The location of Rh, which shows as bright contrast, is seen on Fig. 2C. The EDS analysis of one of such location is presented on Fig. 2D, where Rh L-lines appear on the spectrum between 2.5 and 3.0 keV. The agglomeration of Rh on the grain boundaries may result from a thicker solution film residue from the impregnation, or reflect that the interaction between Rh and the support is stronger at these sites. Beside alumina (peaks of aluminium and oxygen), EDS identified carbon originating from the coating applied to prevent charging and contamination. Clusters of Rh particles could also be found on top of the alumina particles. The diameter of these clusters was typically 0.2–0.6 µm. The EDS analysis of a representative Rh cluster is shown in Fig. 2E.

Fig. 3 show the results of FE-SEM analysis of a 0.01wt.% Rh/Al_2O_3 foam exposed to POX reaction conditions. The alumina particles clearly undergo structural changes under these conditions. A high number of larger alumina particles were observed (Fig. 3A). Fig. 3B also shows the alumina particles to have different shape and surface morphology compared to before the reaction experiments (Fig. 2B). The alumina surface contains several round-shaped features (pits or mounds) that were not previously observed.

A backscattered electron image of a sample used in POX is shown in Fig. 3C. Rh particles were observed not only between alumina particles but also on their surface. The diameter of the Rh particles in Fig. 3C vary from 0.014 to 0.086 μm, and particles of such size and density were not found on unused Rh foams. It appears unlikely that these quantities of Rh has agglomerated from a thin surface layer or highly dispersed particles that could not previously be detected on the surface. This means that the Rh solution probably penetrates into the internal structure of the alumina during preparation. The solution may enter the internal structure through the grain boundaries and small openings between the alumina crystallites, or through the rather large hollow channels observed inside the interconnected alumina ‘‘fibers’’. During the POX experiments, Rh then migrates to the surface of the macropores and sinters into large particles.

Changes in Rh particle size and distribution were even more pronounced on the foam used for OSR. Higher number of Rh particles were found on this sample (Fig. 4A) compared to the one used for POX, with the highest density along the grain boundaries between alumina particles (Fig. 4B). Thus, these constitute preferential sites for such particles. Also the Rh particle size was larger, with diameters up to 0.27 μm (Fig. 4C), pointing to increased tendency to sintering upon exposure to steam at high temperature.

The highest degree of structural change was observed on the catalyst subjected to the reaction conditions that caused the most significant loss in activity, i.e. OSR. High concentrations of steam thus seem to have stronger impact on the stability of Rh than high temperatures in themselves. Steam is formed during POX, and could possibly contribute to changes and reduced selectivity to desired products during time-on-stream. However, oxygen is present in both experiments and its contribution to the particle modification cannot be ruled out. The conditions on the feed side of the foam are the most extreme with respect to oxidative potential, and it is not possible from experiments or characterisation to conclude whether it is actually Rh or Rh oxide that is involved during restructuring. Finally, the structural changes observed in the alumina foam itself could also be involved in the loss of catalytic activity.

Longer time-on-stream experiments are needed to establish whether the structural changes can be stabilised. The application of this relatively simple catalyst system points to which parameter is the most problematic with respect to deactivation, i.e. the steam content. However, it is by the addition of steam that the hydrogen production in such process can be increased. Future choices of process conditions for hydrogen generation appear to be particularly dependent on whether the catalyst can be made sufficiently stable in the presence of steam.

4. Conclusion

Rh-impregnated (0.01 wt.%) Al_2O_3 foam catalysts are active for both partial oxidation and oxidative steam reforming of propane. The highest selectivity to hydrogen (0.92) relative to propane converted at almost complete propane conversion (0.96) was obtained by oxidative steam reforming at 700 °C. Higher stability and lower selectivity (0.72) of the 0.01wt.% Rh/Al_2O_3 catalyst was observed for POX than for OSR, indicating that the presence of steam in the reaction mixture is the strongest cause of deactivation. The losses in catalytic activity could be ascribed to modification of the Rh particle size and distribution on the alumina foam as analysed by FE-SEM, which were more pronounced after being exposed to oxidative steam reforming reaction conditions.

Acknowledgement

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References

[1] J.L. Williams, Catal. Today 69 (2001) 3.
[2] I.M. Lachman, J.L. Williams, Catal. Today 14 (2) (1992) 317.
[3] R.M. Watwe, B.E. Spiewak, R.D. Cortright, J.A. Dumesic, J. Catal. 180 (1998) 184.
[4] G. Veser, L.D. Schmidt, AIChE 42 (4) (1996) 1077.
[5] M. Fathi, K. Heitnes Hofstad, T. Sperle, O.A. Rokstad, A. Holmen, Catal. Today 42 (1998) 205.
[6] R. Lødeng, O.A. Lindvåg, S. Kvisle, H. Reier-Nielsen, A. Holmen, Appl. Catal. A: Gen. 187 (1999) 25.
[7] B. Silberova, M. Fathi, A. Holmen, Appl. Catal. A: Gen. 276 (2004) 17.
[8] A. Beretta, P. Forzatti, Chem. Eng. J. 99 (2004) 219.
[9] O.V. Buyevskaya, K. Walter, D. Wolf, M. Baerns, Catal. Lett. 38 (1996) 81.
[10] S.S. Bharadwaj, L.D. Schmidt, J. Catal. 146 (1994) 11.
[11] K. Walter, O.V. Buyevskaya, D. Wolf, M. Baerns, Catal. Lett. 29 (1994) 261.
[12] P.M. Torniainen, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.
[13] D.A. Hickman, E.A. Haupfear, L.D. Schmidt, Catal. Lett. 17 (1993) 223.
[14] K.H. Hofstad, J.H.B.J. Hoebink, A. Holmen, G.B. Marin, Catal. Today 40 (1998) 157.
[15] E.P.J. Mallens, J.H.B.J. Hoebink, G.B. Marin, J. Catal. 167 (1997) 43.
[16] K.L. Hohn, L.D. Schmidt, Appl. Catal. A: Gen. 211 (2001) 53.
[17] E. Ruckenstein, H.Y. Wang, J. Catal. 187 (1999) 151.
[18] D.D. Beck, T.W. Capehart, C. Wong, D.N. Belton, J. Catal. 144 (1993) 311.
[19] T. Mizuno, T. Nakajima, J. Chem. Eng. Jpn. 35 (5) (2002) 485.
[20] B. Silberova, H.J. Venvik, A. Holmen Catal. Today, doi:10.1016/j.cattod.2004.09.025.