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## Permeable composite membrane as a catalytically active contactor for hydrogenation reactions

### T.P. Minyukova<sup>a,b,\*</sup>, N.V. Shtertser<sup>a,b</sup>, A.A. Khassin<sup>a,b</sup>, T.M. Yurieva<sup>a</sup>

<sup>a</sup> Boreskov Institute of Catalysis, 5 pr. Ak. Lavrentieva, Novosibirsk 630090, Russia <sup>b</sup> Novosibirsk State University, 2 ul. Pirogova, Novosibirsk 630090, Russia

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### ABSTRACT

The efficiency of using of the permeable composite membrane (PCM) is demonstrated in the 3-phase reaction of liquid substrate with gaseous hydrogen on solid catalyst (PCM acts as a catalytically active contactor)-hydrogenation of fatty acid triglyceride. PCM provides a good combination of the opposite requirements of mild internal diffusion restrictions, low hydraulic resistance, high thermal conductivity, well-developed gas-liquid interface and high catalyst loading in the reactor volume, and thus assures the control of the course of the catalytic reaction.

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### 1. Introduction

A three-phase exothermal catalytic process (e.g. hydrogenation) is hindered by mass-transfer restrictions at the gas-liquid interface as well as by internal diffusion in the flooded pores of the catalyst grain. Hot spots in the dry zones of the catalyst at the proximity of the gas-liquid boundary may cause poor selectivity and even lead to the process runaway. At that, hydraulic resistance of the partially wetted catalyst bed may become severely inhomogeneous, while the process productivity and selectivity decrease in the stagnation zones. Therefore, the requirements of intense internal diffusion, well developed gas-liquid interface, low and uniform hydraulic resistance, high thermal conductivity, and high catalyst loading must be simultaneously fulfilled.

This is a sophisticated task. Slurry reactors, including slurry bubble column reactors (SBCR) and slurry stirred tank reactor (SSTR), are often used. However, the slurry reactors need catalyst separation, which is not easy. Also, SBCR reactors are characterized by a very low catalyst loading below 15 wt.%, since higher concentration of the particulate matter causes coalescence of gas bubbles and critically decreases gas-liquid interface. The pore-through-flow membrane reactors, used in some hydrogenation reactions [1,2] allow to exclude the mass transfer limitations. In reviews [3,4] it is concluded that the potential of the reactors in flow-through mode both for gas and liquid phase reactions is high, but the isothermal operation can hardly be enabled for strongly exothermic reactions. Rather low content of the catalytically active component in the unit of the reactor volume and limited stability are another disadvantages of the pore-through-flow membrane reactors.

Stable operation of the process at the gas-liquid interface may be achieved by using contactor membranes, as it was earlier proposed for hydration of propene [5], aqueous nitrate reduction [6], multiphase  $\alpha$ -methylstyrene hydrogenation [7].

As suggested in [8–12] plug-through permeable composite membranes (PCM) for Fischer-Tropsch synthesis meet all the requirements of the process. They have high heat conductivity (isothermal regime of the catalyst bed), high mechanical strength and high active component loading in the unit volume. Surely, like other plug-through contactors they possess high permeability for the gaseous and liquid reactants, the homogeneity of the catalytically active substance distribution in the body of PCM, arranged porous structure, providing mass transfer and diffusion control in the course of reaction. For Fischer-Tropsch synthesis such an approach allowed to achieve high productivity of reactor and high selectivity of the process together with flat temperature profile across the membrane and reasonable pressure drop.

Same type of PCMs was successfully applied in the 2-phase reaction of two gaseous reactants on solid catalyst, where PCM acts as controller of an internal diffusion and heat transfer in a structured catalyst bed-preferable CO methanation in CO<sub>2</sub> containing hydrogen-rich gas [13,14]. For inlet gas composition  $CO:CO_2:H_2:H_2O = 1:21:60:18$  the PCM based on NiCr oxide catalyst provides the fine purification down to residual CO concentration of 10–30 ppm in the wide range of GHSV from 6000 to  $17,000 \text{ h}^{-1}$  and ensures the selectivity above 0.5 at atmospheric pressure and in



<sup>\*</sup> Corresponding author at: Boreskov Institute of Catalysis, 5 pr. Ak. Lavrentieva, Novosibirsk 630090, Russia. Tel.: +7 383 330 91 09; fax: +7 383 330 80 56. E-mail address: min@catalysis.ru (T.P. Minyukova).

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### Table 1 Characteristics of catalytically active components.

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Catalyst	Cu loading (at.%)	Activation temp. (°C)	Phase composition after activation	Me <sup>0</sup> particle size
CuZn(O) CuCr(O)	8 <sup>a</sup> 33	350 350	Cu <sup>0</sup> /a.m.ZnO Cu <sup>0</sup> /H <sup>+</sup> -spinel	3–5 nm 5–10 nm

<sup>a</sup> (Cu + Zn) = 100 at.%.

the temperature range of 195–215 °C. PCM was 18 mm in diameter and 13 mm in height.

In the present study it is demonstrated that possessing these properties provides the efficiency of using of the PCMs in the 3-phase reaction of liquid substrate with gaseous hydrogen on the solid catalyst (PCM acts as a catalytically active contactor)—hydrogenation of fatty (stearic) acid triglyceride.

#### 2. Experimental

Transformation of triglyceride of stearic acid was carried out over the PCM contactor membranes based on Cu-containing catalytically active substances and over immersed granulated Cu-containing catalyst. The procedure of PCM preparation was described earlier in [9]. The PCM is prepared from a threecomponent mixture of (1) a catalytically active substance, (2) reinforcing metal with high heat conductivity and (3) poreproducing agent.

- (1) We used appropriate mixed hydroxocarbonates as a catalytically active substance precursor. The size of granules was 0.15–0.25 mm, the catalytically active component loading was 1.5 g. The characteristics of used catalytically active components are presented in Table 1.
- (2) Dendritic copper was used as a reinforcing component for PCMs, since it is rather inert with respect to hydrogen, water vapors and other reactants and also it has a reasonable Tammann temperature (of about 410°C).
- (3) Copper hydroxocarbonate (malachite) was used as pore producing agent.

Finely mixed three component mixture is pressed in a form of a hollow cylinder of 18 mm in an outer diameter and 12 mm in a height, sintered and reduced in flowing hydrogen. So, the obtained a permeable membrane that provides a gas flow permeating via a set of the partially wetted transport pores. The direction of gas flow is radial, from the center to the outer surface. Reverse flow from the outer surface to the center is also possible. Fig. 1 shows the appearance of the PCM.

By optimizing the composition and conditions of the PCM membrane preparation, we managed achieving high permeability of ca. 300 mDarcy (causing low pressure drop), high catalyst loading of ca. 1 g/cm<sup>3</sup> (the same as for fixed bed reactor), high heat conductivity of 1-4 W/(m K) (causing isothermic regime of reactor), small effective size of catalyst grain of 0.15–0.25 mm (mild diffusion constrains) and well developed pore structure (causing enhanced gas–liquid interface) [9].

We used a specially designed reactor for PCM testing; the scheme of this reactor is shown in Fig. 2. The direction of hydrogen is from the center to the outer surface. The PCM is immersed in the liquid triglyceride. Rather intensive hydrogen flow prevents the filling the transport pores with liquid. This type of reactor and regime of its operation is suitable only for the reagents having similar physical properties. The initial stearic acid triglyceride volume was 21 ml, hydrogen flow – 7 l/h, reaction temperature – 340 °C, pressure – 2 MPa. Reaction time was 3 h.



Fig. 1. Permeable composite membrane (PCM-cylinder) for triglyceride of stearic acid hydrogenation. The height is 12 mm, outer diameter – 18 mm.

A mixture of  $C_{18-17}$ -alkanes, alkenes, alcohols and acids as well as some  $C_{18}$ - $C_3$  and  $C_{18}$ - $C_{18}$  esters is found downstream in the condenser. After cooling, the hydrocarbon mixture in reactor is enriched in high-boiling products. Volatile products of hydrogenation evaporate and condense downstream.

The analysis of the products was performed by the specially developed accumulative NMR method. NMR spectra of dissolved in CDCl<sub>3</sub> or CCl<sub>4</sub> probes of the reaction products were recorded at Bruker Avance 400 at 400.13 MHz (<sup>1</sup>H) and 100.61 MHz (<sup>13</sup>C).



Fig. 2. Scheme of PCM reactor for triglyceride of stearic acid hydrogenation.



Fig. 3. Triglyceride of stearic acid hydrogenation main products distribution, obtained on granulated CuZn catalyst and PCMs, based on CuZn and CuCr oxide catalysts.

### 3. Results and discussion

The results of analysis of the products, obtained on the granulated CuZn oxide catalyst (1.5 g, as in PCM) and PCMs, based on CuZn and CuCr oxide catalysts are presented in Fig. 3. The high conversion of 92–99% was achieved in the experiments.

The set of the reaction products obtained on the granulated catalyst and on the catalyst in the form of PCM is the same, probably owing to the same catalytically active component—copper. The main products are  $C_{18}$  hydrocarbons,  $C_{18}-C_{18}$  ester,  $C_{18}$  alcohol and  $C_{18}$  acid. The result obtained in the present study for the granulated CuZn catalyst is in accordance with the literature data [15]. Saturated and unsaturated  $C_{18}$  hydrocarbons are the main products of stearic acid triglyceride hydrogenation on granulated CuZn oxide catalyst, small amounts of  $C_{18}$  – alcohol,  $C_{18}-C_{18}$  – ester and  $C_{18}$  – acid are observed. Hydrocarbons are also formed on PCMs, while oxygen containing products are formed in significant amounts. Comparing the product distribution for PCM based on different active component it may be noted that the rate of the ester formation is higher for CuZn-PCM than for CuCr-PCM.

It is known from the literature [15,16] that in traditional reactors (tubular or multiple-shell reactor) under the action of hydrogen at increased pressure and temperature triglyceride of stearic acid hydrogenation occurs on sprinkled or immersed Cu-catalysts according to the scheme, presented in Fig. 4, and that the main products are alcohol and hydrocarbons.



**Fig. 4.** The scheme of triglyceride of stearic acid hydrogenation on the granulated Cu–Zn oxide catalyst [15,16].

The obtained products composition makes it possible to assume, that triglyceride of stearic acid hydrogenation on PCMs occurs via another scheme (Fig. 5). The proposed scheme shows the way of stearyl stearate formation. Stearyl stearate is an intermediate product, which can be transformed into the alcohol and acid and then can be hydrogenated according to the scheme in Fig. 5. It is well known from the literature [1,17] that membrane reactor provides the set of conditions for achieving the high selectivity to the intermediate product of the consecutive reaction.



Fig. 5. Proposed scheme of triglyceride of stearic acid hydrogenation on PCMs.

So, the use of PCM for triglyceride of stearic acid hydrogenation opens possibility for formation of rather valuable products, such as  $C_{18}-C_{18}$  ester.

### 4. Conclusion

It is shown that Cu-based PCMs provide the control of the direction of the catalytic reaction triglyceride of stearic acid hydrogenation. By varying the composition of PCM active component and the conditions of reaction it is possible to transform the triglyceride of fatty acid to valuable chemicals, as fatty esters of higher alcohols. With their high heat conductivity (isothermal regime of the catalyst bed), high mechanical strength, high active component loading in the unit volume and easy separation from the reaction products Cu-based PCMs may have very god potential as a catalysts for triglyserides of fatty acids transformations.

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