

A new type structural catalytic carrier and system for selective oxidation of gaseous hydrocarbons

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Abstract

Over the last few years the micro-method achievements have emerged as the high-throughput experimentation approaches to complex processes in which development of heterogeneous catalysts for industrial purposes has become a challenge. Also the selective oxidation of gaseous alkanes should be directed towards green and profitable synthesis which involve complex processes. Namely, intermediates of the high activation-temperature oxidation react faster than the alkane substrate and burn up especially at hot-spots due to temperature rise and catalyst deactivation. Moreover, uniformity between alkane functional groups complicate the oxidation scheme with parallel side-reactions. However, in this case the well-known, adverse effect of unsatisfactory comparability of the micro-method with those obtained in the conventional reactors becomes a problem that permanently follows a limitation of heat-transfer across catalytic grains. The limitation causes non-isothermal conditions and then the hot-spot effects which give rise to the incomparability. Hence, to date n-butane selective oxidation to maleic anhydride on VPO phases is the only such a synthesis applied on the industrial scale owing to both stability of the quasi-aromatic product and selectivity of the catalyst acting as a stoichiometric agent that for this reactivity is used only in grain forms. Accordingly, a short contact-time, selective catalytic system could bring about the comparability and then selectivity. Therefore, a new catalytic system of thin-layer VPO catalyst on structured carriers with enhanced heat-transfer efficiency was elaborated in this work, and optimized towards n-butane selective oxidation on a semi-industrial scale. The selective oxidation on that catalyst was controlled with the intrinsic process parameters and reactant properties. On the other hand, it is well-known that isothermal micro-processes are controlled with the same parameters and properties. In a consequence, the thin-layer catalyst was supported on structured gauze for research on the selective oxidation of gaseous alkanes under the comparability conditions.

Key words: selective oxidation, light alkanes, maleic anhydride, structural carrier, VPO catalyst, HTE

Introduction

Consecutive effects that influenced the catalytic activity and selectivity of the fixed beds process were analysed for the highly exothermic gas-phase selective oxidation of hydrocarbons in terms of the heat dissipation, hot spot behaviour, structure-reactivity relationship, and incompatibility between micro- and practical-scale process parameters. Thus, new structured forms of catalytic carriers were designed against the adversely influences, and then prepared and optimized for heat and mass transfer enhancement. Then, a new thin-layer vanadium-phosphorus oxide catalytic system was elaborated on the carrier surface with XRMF and SEM controlling. The thin-layer system was tested with MS/GC as catalyst for n-butane selective oxidation. It was apparently controlled with the intrinsic parameters of the process. Finally, the thin-layer system was developed into new, metal-gauze supported catalytic system for the process research and extension. These results suggest the promise of novel synthetic possibilities, via the selective oxidation of naturally abundant and low cost light alkanes, by the access to the intrinsic process parameters which could be transferred from the high-throughput experimentation microreactors to the conventional scale fixed bed reactors with the metal gauze supported thin layer vanadium-phosphorus-oxides as the catalyst.

Currently, disproportion was growing between potential of the high-throughput experimentation (HTE) for speeding up discovery of the catalyst and their subsequent application to selective oxidation of gaseous hydrocarbons on the practical scale. On the other hand, the hot-spot effects in the fixed-bed catalysts cause incompatibility between the above catalytic systems: experimental and practical.

It was decided to overcome the above problems by means of structural carriers and relevant thin-layer VPO catalyst for n-butane selective oxidation. Therefore, a new preparation method of the supported, active and selective vanadium-phosphorus-oxides catalyst (VPO) on structured carriers was investigated and tested with XRMF, SEM and MS/GC. This catalytic system was developed into new, metal-gauze structured, VPO system for selective oxidation of gaseous hydrocarbons, compatible with the HTE technique.

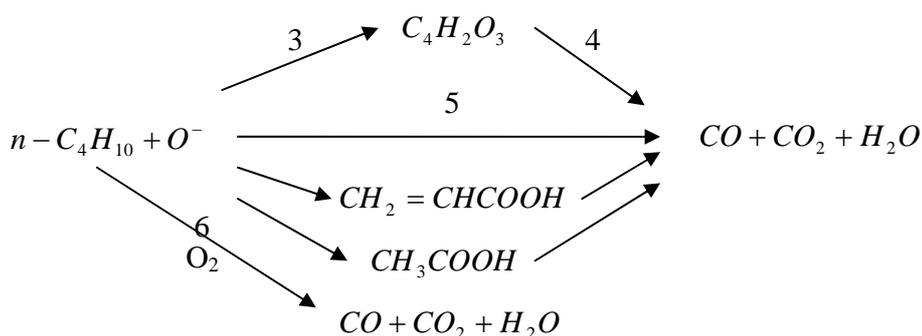
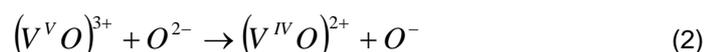
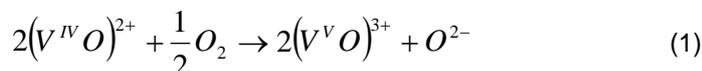
Over a couple of past years disproportion was growing between potential of the HTE and lack of catalysts for selective oxidation of light alkanes to valuable reagents via both green and profitable processes. To date, n-butane (BuH) oxidation to maleic anhydride (MA) on VPO catalysts is the only such a synthesis applied on the industrial scale. However, HTE technique in the case of BuH has received no attention as yet.

Currently, there perform three main catalyst types for selective conversions of light alkanes: heteropolyacids, mixed metal oxides and VPO [1]. Nevertheless, selectivity at the high-temperature activation of the hydrocarbons is still low, and then intermediates react faster than the hydrocarbon substrate. Additionally, heat-transfer limitations on such highly exothermic oxidation processes and hence the hot-spot effects influence catalytic performance of the fixed beds [2], mask the structure reactivity relationship and then cause incompatibility with HTE micro-reactors which could enable to tune the catalytic performance of the beds.

Therefore, in this work we developed VPO catalyst into a system compatible with both HTE technique and industrial practice.

Theoretical

According to the results of the process investigation (Figs. 3, 4), the following network of the selective oxidation of BuH on TLVPO catalyst can be introduced:



Experimental

Preparation of the structural carrier and measurements for establishing their heat-flow characteristics were presented previously [3].

A number of elaborated structures and a few of common structures (Fig. 1) were tested according to the previously introduced criteria [4] (Fig. 2).

Preparation of thin-layer vanadium-phosphorus-oxides (TLVPO) catalyst follows in a three-stage procedure with XRMF and SEM controlling.

In this 1st stage, the carrier was calcined in a muffle furnace at temperatures 1000-1050°C during 110 h. As a result the carrier surface was covered with 0.5-1 μm crystallites of γ - Al_2O_3 primer. In the 2nd stage, on the primer an alumina-titania support was laid by dipping in Al-Ti hydroxide colloidal dispersion and then drying a wash-coat thus formed at 90°C for 1 h. Such impregnation was repeated 3 times and each of the

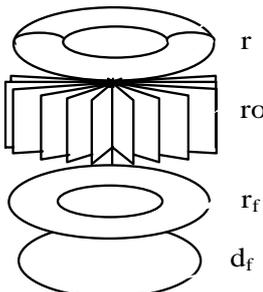
successive wash-coats was heated at 500°C for 2 h. As a result, the support layer has been deposited with 5 μm thickness and surface density of 1.9 mg cm^{-2} . In the 3rd stage, a precursor of the VPO catalyst was made from ammonium metavanadate and phosphoric acid via a suspension formed in aqueous glycerol (20 w/w % of water). The carrier with the support layer was immersed in the suspension and then dried at 180°C for 5 h. The process of this coverage was repeated 3 times and then the precursor underwent heating in oxygen atmosphere. The heating temperature was raised for 3°C/min., and then was maintained at 500°C for 3 h. Finally, the carrier with the precursor layer was cooled at 4 °C/min. Smooth structure can be covered uniformly and repeatedly, with surface density of 0.8 mg cm^{-2} , and proper and heating-resistant P/V ratio, compact and well-formed micro-crystallite structure. Contrary, preparations on sharp structures formed VPO layers that underwent the phosphorus losing on the heating.

The TLVPO catalyst has been formed with in situ activation of the above precursor by heating on the reactant stream for constant concentration of maleic anhydride and the other reactants.

After elaboration of the equilibrated catalytic system, a testing phase follows applying the previous methods [3]. In this phase, stability,

activity and selectivity of the equilibrated TLVPO catalyst were studied on the pilot-plant scale chosen between laboratory and practical scale. The results are presented in Figs. 3 and 4 wherein each experimental point represents the mean of data from three independent runs on the equilibrated catalyst prepared on the rosette surface (Fig. 1).

Type	Carrier
H1	Hband ^b
H2	Hwire ^c
H3	Hwire ^d
H4	Hscrew ^e
P1	Pceram. ring ^f
P2	Pceram. ring ^g
P3	Pmetal. ring ^h
P4	Pmetal. ring ⁱ
P5	Pmetal. ring ^j
R1	(s in ro)
R2	(ro+r _d)
R3	(ro+r)
R4	(ro+r _f)
R5	(ro+r _d +ro+d)
R6	(ro+r _f +ro+d _f)
R7	(ro+ro+r _d)
R8	(ro+ro+r _f)



^a H – helical, P – Raschig ring, R – modular, of CrAl steel-foil, composed from the above elements:
ro(rosette of 20 leaf), de/h/t=26.0/10.0/0.05;
s (streamline core), de/h=11.8/19.1;
r_d (drawed U-ring), de/di/h/t (external diameter/internal diameter/high/thickness, mm)=24.3/14.1/2.0/0.30;
r (U-ring), de/di/h/t=24.4/12.0/2.2/0.30;
r_f (flat ring), de/di/t=25.3/16.0/0.30;
d (disk), de/h/t=20.0/3.3/0.30;
d_f (flat disk), de/t=23.0/0.30;
^b A helical structure of a metallic band, de/di/h/t=19.0/13.0/24.0/0.5;
^c A helical structure of a coiled wire, de/d_{coil}/t=24.4/7.8/0.56;
^d The helical structure of the coiled wire, double;
^e A helical structure of the metallic screw, de/di/h/t=24.3/10.0/7.5/0.5;
^f The ceramic Raschig ring with rounded edges, de/h/t=7.0/7.0/1.5, randomly packed;
^g The ceramic half-ring, de/h/t=10.0/6.0/2.0, randomly packed;
^h A metal Raschig ring, de/h/t=5.1/5.0/0.25, randomly packed;
ⁱ The metal Raschig ring randomly packed round a core, d_{core}=13.8;
^j The metal Raschig ring put in alternate order round the core;

Fig. 1. The structured carriers.

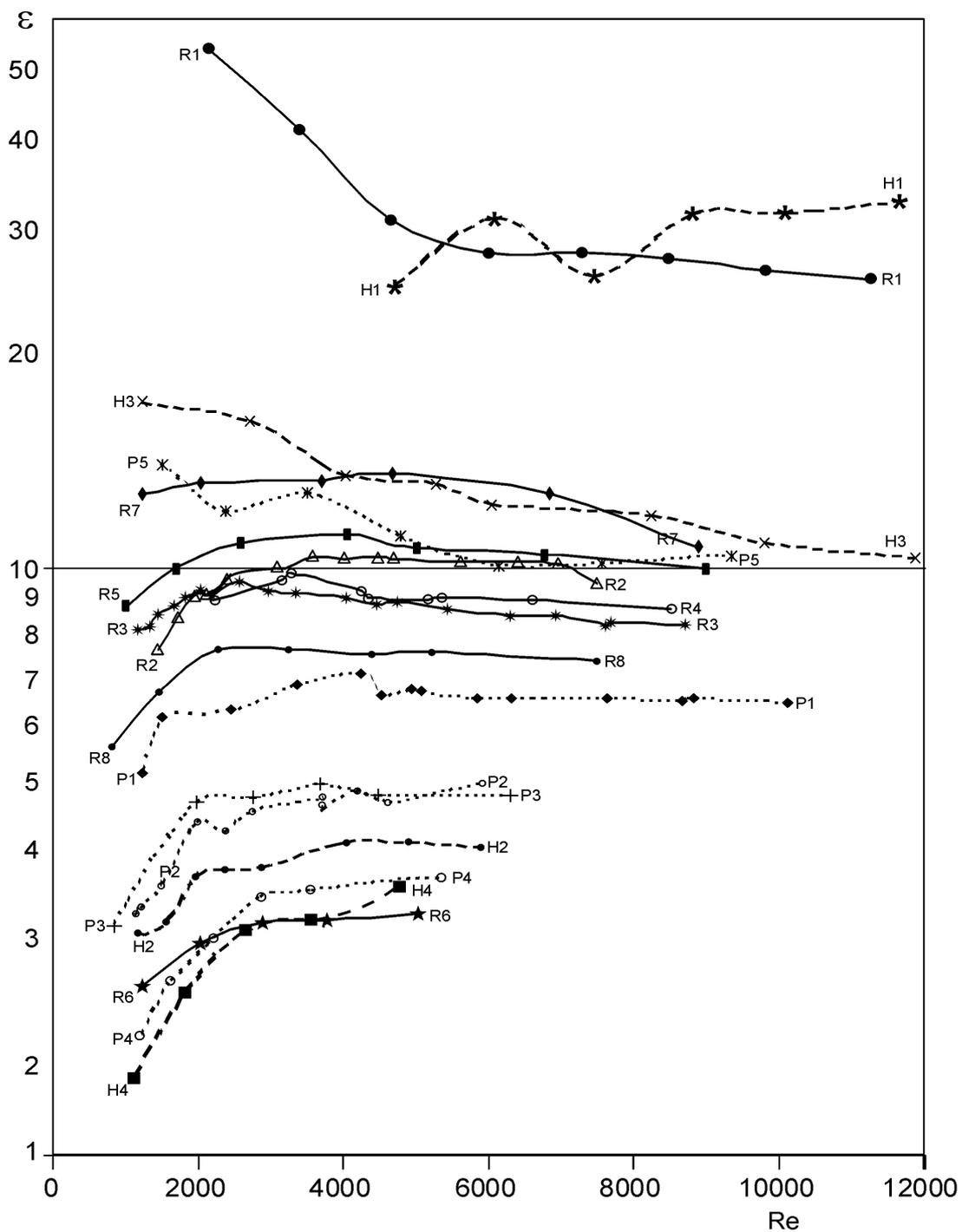


Fig. 2. The heat-flow efficiency of the structured carriers under conditions closely related to the process conditions

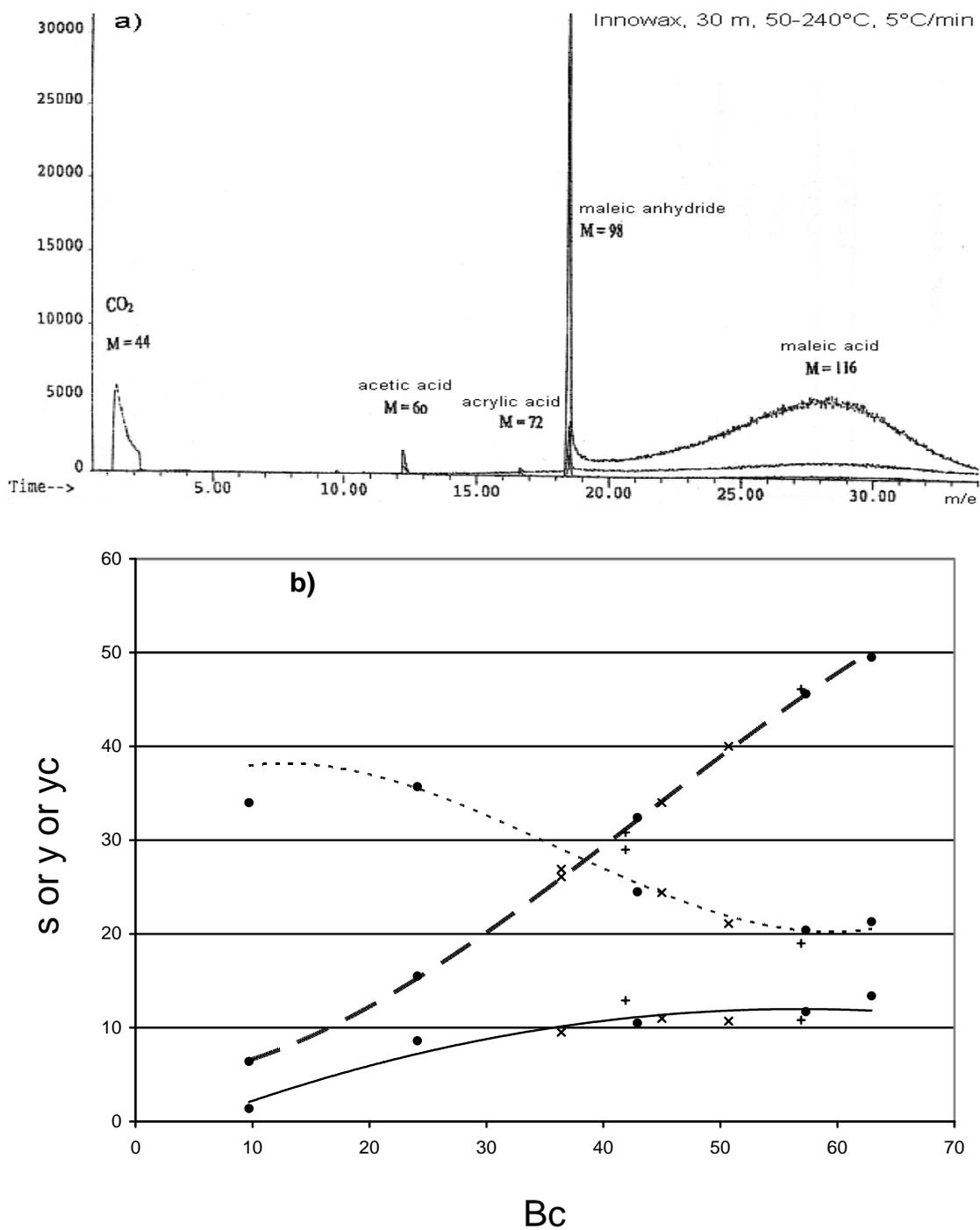


Fig. 3. The process products (a), and general characterizing (b): (—) y, (.....) s, (---) yc, (—) Bc, (○) at 360 °C, (●) at 370 °C, (x) at 380 °C, (+) at 390 °C.

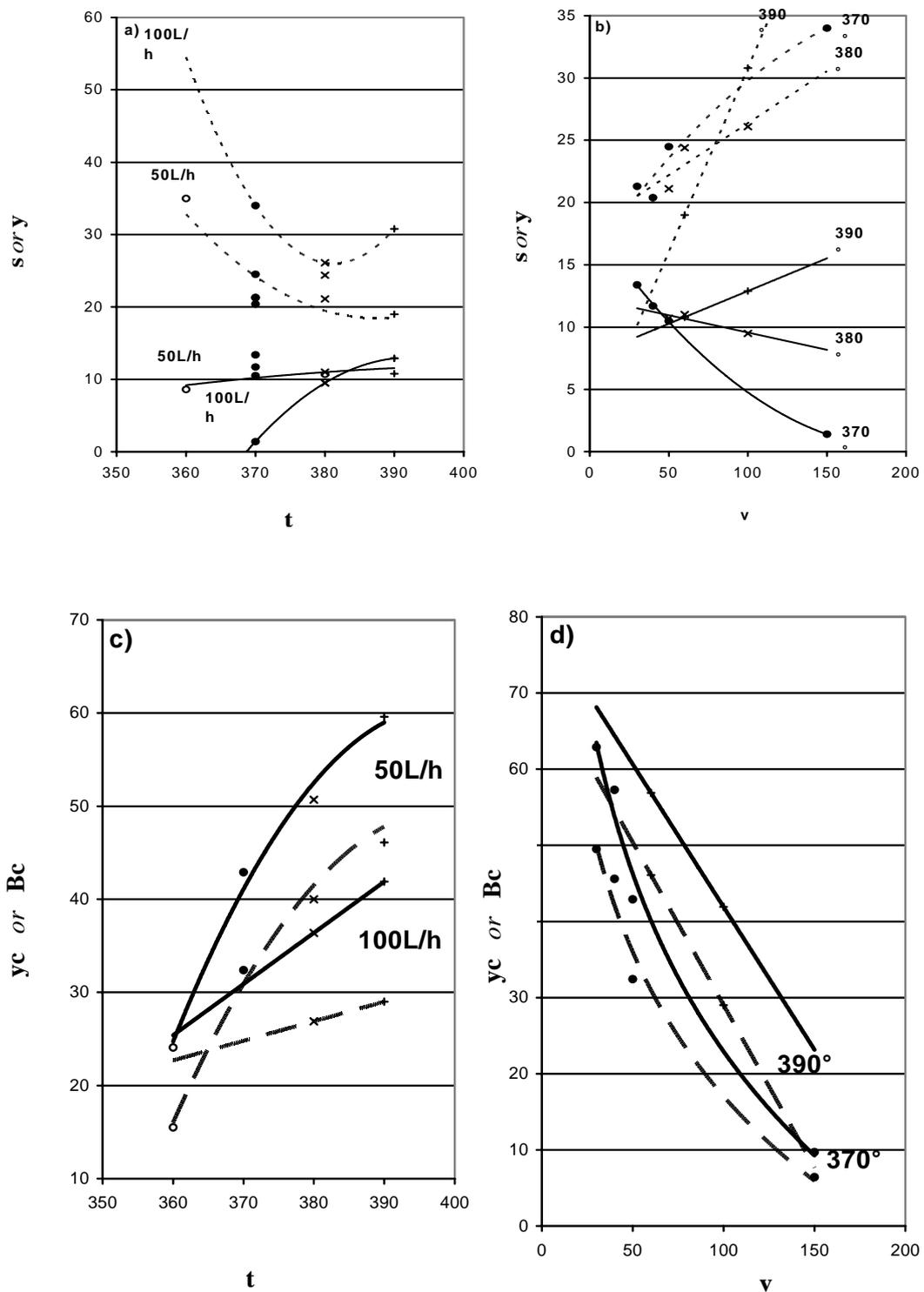


Fig. 4. The process characterizing

Result and discussion

The TLVPO catalyst on the structural carrier performed as an active and stable system that formed MA, final oxidation products as well as intermediate by-products, acrylic acid and acetic acid (Fig. 3). It was noteworthy the detection of the above intermediate. Apart from MA no intermediate was detected to date in the equilibrated reactants of the BuH oxidation with air on active VPO catalysts under the oxidizing conditions and at atmospheric pressure (i.e. under this work conditions) because of their total oxidation before desorption from the known VPO catalysts (i.e. grains). This desorption properties on TLVPO catalyst enable us to study the process with intrinsic parameters. The process variable derived relationships in the case of MA differ diametrically from those for carbon oxides (Figs. 3b, 4). The selectivity in MA did not decreased with the process temperature (Fig. 4a, b), whereas on the other VPO catalysts detrimental effect of rising process temperature has been observed, e.g. [5]. Then, the results ranged over the above relationships indicate consecutive oxidation of organic reactants in competition with their desorption (oxidations via O^- in the reaction network). These selective reactions performed according to the intrinsic parameters closely related to the chemical reactivity in the network. Additionally, on the unselective sites reaction 6 occur.

On the other hand, both yield and selectivity in MA were low and unacceptable in terms of practical requirements because TLVPO could catalyse in MA only a small fraction of BuH feed (Fig. 3b). However, efficiency of TLVPO catalyst has attained 0.7 g MA / 1 g catalyst · 1h. This is considerable higher than the efficiency that has been presented for the other VPO catalyst under the oxidizing conditions [6]. As another example,

we have found that 10 times more of the VPO catalyst on porous ceramic rings formed in comparison with TLVPO catalyst 5 times more MA at the efficiency 0.35 g MA / 1 g catalyst 1 h. Because in the case of VPO catalysts the number of catalytically active layers is limited to a few top layers [7], the catalyst re-oxidation steps (reactions 1, 2) were decisive here. Indeed, the activation energies of the VPO catalyst redox cycle have already been determined at 157.4 kJ·mol⁻¹ and 199.4 kJ·mol⁻¹ for reaction 1 and 2, respectively [8]. They are more than the activation energies of the organic oxidations: 93.1 kJ·mol⁻¹ (reaction 3 or 4) and 155 kJ·mol⁻¹ (reaction 5) [6]. However, in a way to overcome such problem with development of the carrier structure the unavoidable both thermal and flow limitations on the carrier efficiency were found [4]. Therefore for the catalytic carrier development, only a few of the structure-performance relationships shown in Fig. 2 could be applied. There were the following relationships:

- the streamline structures are generally more effective than sharp-structured internals (R1 vs. R2, R3, R4; H1 vs. H4; P5 vs. P4; P1 vs. P2);
- the axial-vortex motion promote the efficiency (H1 vs. H2);
- the structure features may be decisive over material properties (P1 vs. P3, P4);
- helical, structures may be very efficient (H1, H3, P5).

These relationships may be interpreted in terms of considerable convection of the reaction heat with the reaction stream.

As the result, a structured metal-gauze carrier has been introducing, and covered with either alumina or quasi-zeolite primer [9], for preparation of a new TLVPO catalyst [10]. This system is potentially compatible over the above process scale.

Symbols

BuH	n-butane	
HTE	high-throughput experimentation	
MA	maleic anhydride	
R	Reynolds number	
s	selectivity in maleic anhydride	mol %
TLVPO	thin-layer vanadium-phosphorus-oxides	
t	temperature	°C
v	volumetric flow rate of the process stream	dm ³ ·h ⁻¹
y	yield of maleic anhydride	mol %
yc	yield of carbon oxides	mol %
Bc	conversion of n-butane	mol %

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