Influence of the Pressure on the Product Distribution in the Oxidative Dehydrogenation of Propane over a Ga$_2$O$_3$/MoO$_3$ Catalyst

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Influence of the Pressure on the Product Distribution in the Oxidative Dehydrogenation of Propane over a Ga_2O_3/MoO_3 Catalyst[*]

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Abstract

The yields and selectivities in both the catalyzed and non-catalyzed oxidative dehydrogenation of propane were found to increase with increasing pressure. The results showed that the maximum yields of valuable ODH products could be obtained by adjusting only reactants' partial pressure, while keeping their ratio constant.

KEYWORDS: oxidative dehydrogenation, heterogeneous catalysis, process development

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1. INTRODUCTION

The *oxidative dehydrogenation* of propane as an alternative route for the production of propylene is drawing increasing attention due to the increasing demand for lower olefins. The present production capacity mainly consists of steam crackers, which are usually operated to obtain maximum ethylene yields. (Dharia et al., 2004)

The main alternatives are the dehydrogenation and oxidative dehydrogenation (ODH) of propane, with the first one taking place at high temperatures of $800 - 900\,K$ to obtain a favorable thermodynamic equilibrium. (Gussow et al., 1980) However, a high reaction temperature also leads to coke formation and cracking to ethylene, which both can be avoided with the ODH reaction. (Albonetti et al., 1996; Koc et al., 2005) In this process, which can for example be catalyzed by Ga_2O_3/MoO_3 mixtures, the main products are, besides propylene and ethylene, methane, carbon monoxide, carbon dioxide and water. Ga_2O_3/MoO_3 catalyst was chosen because of its good performance (good alkane activation properties caused by Ga_2O_3 combined with a partial oxidation behavior of MoO_3, as stated by Davies and Taylor (2004)) and ease of preparation, described in section 2.

A problem in the further development of this system is the deep oxidation to CO_x. The actual mechanism of the overall process is still not known, while the fact that oxygen presence is the key for achieving the conversions beyond those expected based on the equilibrium of the simple dehydrogenation reaction is widely accepted. Although many different and rather complex mechanisms for this reaction are investigated, as presented in Grabowski (2006), the reaction can be simplified to the network shown in Figure 1. (Leveles et al., 2003; Chen et al., 2001)
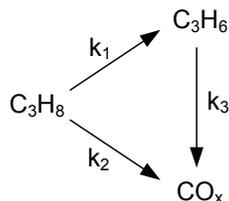

Figure 1: Reaction network for the oxidative dehydrogenation of propane

As already shown by Grabowski (2006), partial pressures of reactants determine the reaction kinetics, therefore also the conversion and selectivities. Changing total pressure while keeping feed composition constant gives us a possibility to explore how conversion and selectivities change with partial pressure change, maintaining their ratio constant.

In attempts to find a catalyst which would both be active at low temperatures and avoid deep oxidation, various materials such as supported molten salt catalysts (alkali chlorides), LiOH/LiI melts, metal sulphates and phosphates, as well as nickel molybdate, niobium pentoxide and TS-1 were investigated. (Fox and Lee, 1973; Dahl et al., 1991; Ushkov et al., 1988; Takita et al., 1989; Mazzocchia et al., 1991; Smits et al., 1991; Schuster et al., 2001) In this paper the influence of pressure on the yields and selectivities in the ODH of propane over a Ga_2O_3/MoO_3 catalyst will be investigated.

2. EXPERIMENTAL

For catalytic experiments, an equimolar mixture of Ga_2O_3 (Aldrich, 99.99 %) and MoO_3 (Aldrich, 99.99 %) was ground in a pestle and mortar, after which tablets were pressed, which were crushed and sieved to obtain a particle size of $0.85 - 1.00\,mm$. Subsequently, the catalyst was calcined at $873\,K$ for 3 hours in an oxidizing helium/oxygen (1:1 volume ratio) atmosphere.

Experiments were performed in a stainless steel packed bed reactor of $70\,cm$ length, equipped with a quartz liner of $10\,mm$ in diameter to avoid possible side reactions with the steel reactor walls. The reactor was heated with two separate electrical ovens controlled by Eurotherm 91e controllers [K-type Chromel™/Alumel™ thermocouples]. A catalyst bed with a volume of $4\,ml$ ($1.1\,g$ of catalyst) was used for all experiments. A gas mixture consisting of helium/propane/oxygen in a volume ratio of 8:2:1 was fed to the top of the reactor with a total flow rate of $110\,ml/min$ using Brooks® 5850TR mass flow controllers. For non-catalytic experiments a similar volume of quartz beads was

used to maintain the space velocity and contact time. Schematic overview of the experimental setup used for this research is given in Figure 2.
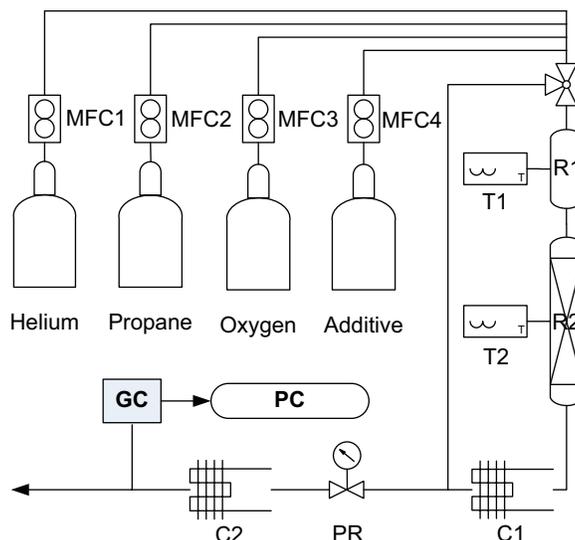

Figure 2: Schematic overview of the experimental setup used in this research: R1–2 — Reactor sections, MFC1–4 — Mass flow controllers, T1–2 — Temperature controllers/indicators, C1–2 — Condensers, PR — Pressure regulator, GC — Gas chromatograph

Experiments were carried out at 733 K and 773 K, varying the pressure from 1 to 6 bar in steps of 1 bar. After each experiment of 5 hours the catalyst bed was regenerated for 2 hours at 873 K with a 1:1 helium/oxygen mixture to remove any coke formed during the reaction. Reaction products were analyzed online on a Varian MicroGC 4900 equipped with both a Molsieve 5 Å and a Al_2O_3/KCl column using thermal conductivity detectors. The carbon mass balance in all experiments was $100 \pm 5\%$.

Propane conversion, X_p, has been calculated according to formula

$$X_p = \frac{C_p^0 - C_p}{C_p^0} \tag{1}$$

where C_p^0 and C_p are the concentrations of propane at the inlet and outlet of the reactor, respectively.

Selectivity to product *i* has been calculated according to formula

$$S_i = \frac{\eta_i \cdot C_i^{formed}}{C_{propane}^{spent}} \tag{2}$$

where η_i denotes a stoichiometric factor.

3. RESULTS

Results obtained from experiments performed at atmospheric pressure (see Table 1) were comparable to those of other authors: Grabowski and Słoczyński (2005) obtained a selectivity to propylene of 76.5 % at a conversion of 1.2 % (733 K) and 72.8 % at a conversion of 1.5 % at 773 K, respectively, over VO_x/SiO_2 catalyst. Schuster et al. (2001) reported on a conversion of 19 % with a selectivity to propylene of over 70 % at 823 K, over the titanosilicalite TS-1 catalyst, whereas the best result of Cadus and Ferretti (2002) was a selectivity of 31.8 % at 21.84 % of conversion at 733 K, over Mo-MnO catalysts.

Increasing the pressure from 1 to 4 bar (733 K) led to a significant increase in the conversion from ∼11 to ∼40 mol%; a further increase from 4 to 6 bar led to a decrease of the conversion to ∼26 mol%, whereas at 773 K

an increase in the pressure of 1 to 3 bar led to an increase in the conversion from ~15 to ~45 mol% (see Table 1). A further increase from 3 to 6 bar led to a decrease to ~34 mol%. Non-catalytic experiments at 773 K revealed a similar trend up to 3 bar, where the conversion was only 2.24 % at 1 bar and 41.61 % at 3 bar. Results at 733 K also revealed an increasing conversion $(0 - 29.1\%)$ with increasing pressure. At pressures higher than 3 bar (773 K) the situation was the opposite: the conversion in non-catalytic experiments was $10.3 - 11.7\%$ higher than in catalytic experiments.

Table 1: Conversion and selectivities for the catalyzed (top) and non-catalyzed (bottom) ODHP at 733 and 773 K

pressure, bar		1	2	3	4	5	6	1	2	3	4	5	6
				T = 733 K						T = 773 K			
X, mol%		10.92	13.51	37.33	39.89	32.50	25.91	15.12	32.61	45.48	34.95	27.39	34.34
		0	1.31	15.08	28.01	29.49	29.10	2.24	12.16	41.61	38.55	30.29	40.38
S, mol%	C_3H_6	51.90	52.00	48.70	46.97	37.53	34.40	51.57	52.68	46.81	46.96	42.50	20.14
		0	100	82.71	52.71	54.28	43.04	66.54	75.96	47.53	49.21	27.99	6.19
	C_2H_4	1.73	5.83	11.94	13.56	8.50	7.20	6.79	23.76	17.99	11.99	9.46	4.74
		0	7.80	10.37	12.01	9.08	8.74	2.97	15.60	21.63	22.61	7.51	1.63
	CH_4	0	3.03	6.19	6.22	7.00	11.19	2.08	7.70	7.76	7.72	8.14	10.20
		0	0	1.39	5.81	3.84	5.08	0	5.51	9.66	9.03	8.86	17.51
	CO	55.74	45.55	21.85	20.34	27.18	37.71	42.77	19.96	14.56	14.75	15.36	20.74
		0	0	10.80	26.55	23.11	29.48	5.46	6.79	15.92	12.39	35.44	27.93

A similar change in the conversion was found at 733 K, where the drop in the conversion occurred at pressures higher than 4 bar. The overall conversion in the catalyzed system was about 55 % higher than in the non-catalytic (26.68 % vs. 17.16 %) at 733 K, whereas the conversion under catalytic conditions was about 15 % higher at 773 K than in the non-catalytic (31.64 % vs. 27.53 %). This was probably due to Ga_2O_3, which is a well known promoter for alkane activation. (Iglesia and Baumgartner, 1993; Hargreaves et al., 2002)

The selectivity to propylene based on propane at 773 K remained ~42.5 – 52.5 % over the pressure range investigated, although for non-catalytic experiments the scattering in the selectivity was large in the range ~49 − 76 %. At 733 K, the scattering was even larger, from 34.40 % to 52.00 % for catalytic and from 43.04 % to 100 % for non-catalytic experiments. The presence of MoO_3 in the catalyst bed certainly had a large influence on the selectivity, as MoO_3 is known to be a selective catalyst in the oxidative dehydrogenation of propane. (Meunier et al., 1997)

At 773 K a significant drop in the selectivity to propylene was found at 6 bar for catalytic and 5 and 6 bar for non-catalytic systems. At 733 K the drop in selectivity was not so drastic as for the catalytic system and decreased from 46.97 % at 4 bar to 34.40 % at 6 bar, via 37.53 % at 5 bar. The non-catalytic system showed a constant decrease in selectivity from 100 % at 2 bar to 43.40 % at 6 bar.

The selectivity to ethylene based on propane showed a comparable pattern at 773 K, reaching a maximum of 23.76 mol% at 2 bar, whereas in non-catalytic experiments the maximum selectivity was 22.61 mol% at 4 bar. Both catalytic and non-catalytic systems showed a maximum ethylene selectivity at 4 bar of 13.56 % and 12.01 %, respectively.

As can be seen from Figure 3, the maximum propylene yield was 18.74 % at 4 bar at 733 K and 21.29 mol% at 3 bar at 773 K. In the non-catalytic system a maximum yield of 14.76 % at 4 bar and 733 K, and 19.78 % at 3 bar and 773 K was found.

The ethylene yield, which also is a valuable product, had a maximum of 8.18 % at 3 bar for the catalytic and 8.99 % for the non-catalytic system at 773 K. At 733 K, the yield was found to be lower and reached 3.36 % in the catalytic and 5.40 % in the non-catalytic system at 4 bar. Methane, and, more importantly, carbon monoxide yields only showed a minor increase over the pressure range studied in these experiments. The maximum yields for methane and carbon monoxide were 7.07 % and 12.06 % for the non-catalytic system at 773 K, respectively. At 733 K in both the catalytic and non-catalytic system, as well as at 773 K in the catalytic system, methane and carbon monoxide yields
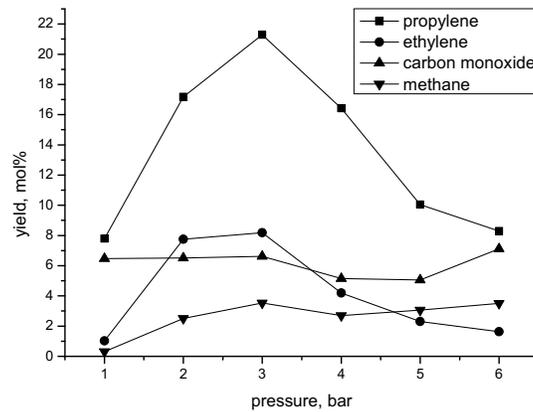
Figure 3: Product yields in the catalyzed ODH of propane at 773 K at different pressures

were significantly lower, with minimum of 1.63 % for methane in the non-catalytic and 2.90 % for CO in the catalytic system at 733 K.

4.   CONCLUSION

The results clearly show that the high yields of valuable ODH products could be obtained by adjusting reactants' partial pressure, while keeping their ratio constant. Maximum yields obtained in this system are comparable to maximum yields obtained from systems using a different catalyst (MgO, Li/MgO, xV/MgO, 18 % yield, Burch and Crabb (1993)) and significantly higher than those obtained from systems with the same catalyst (a 5.7 % yield, Davies and Taylor (2004)).

NOTATION

C	concentration, mol/m^3
ODH	oxidative dehydrogenation
ODHP	oxidative dehydrogenation of propane
S	selectivity, mol%
X	conversion, mol%
Greek Letters	
η	stoichiometric factor
Supercripts	
0	initial value of parameter
Subscripts	
p	propane
i	species i

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