Propane partial oxidation to acrolein over combined catalysts

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A novel approach for the partial oxidation of propane to acrolein, based on the use of layers of combined catalysts in a single reactor, provides good yields of acrolein with selectivity above 62%. The results depend strongly on the layer configuration, and reveal new mechanistic features for the process.

Keywords: propane partial oxidation, acrolein production from propane, combined catalysts, heterogeneous–homogeneous processes, selective oxidation of alkanes

1. Introduction

Selective transformation of low molecular weight alkanes into more valuable products is a challenging task. Oxidative catalytic processes are considered as promising in this sense. Unfortunately, because of their relatively high reactivity the desired product molecules can undergo rapid consecutive overoxidation in the presence of catalysts able to activate even much less reactive paraffin molecules. Up to now the most successful results have been achieved in oxidative dehydrogenation (ODH) of C_2–C_4 alkanes into corresponding olefins. On the other hand, no significant breakthroughs have been made in selective oxidation into oxygenates. In particular, in the case of propane partial oxidation to acrolein (POA), to date the maximum reported yield of the desired product does not exceed 10% per pass (see, for example, [1–4]).

One of the possible reasons why the results are far from desirable is a scarcity of notions about possible pathways of the product formation and, therefore, of ruling ideas for the catalyst design and for the development of the overall process. Indeed, during this complex reaction the initial propane molecule must undergo two types of transformation, dehydrogenation and oxygen insertion, and catalytic systems must carry the two corresponding functions. In principle, there are three possibilities:

(1) simultaneous dehydrogenation and insertion of oxygen into the initial molecule;

(2) sequential dehydrogenation of propane and oxygen insertion into the propene molecule formed;

(3) sequential, but reverse, i.e., oxygen insertion followed by dehydrogenation.

The last possibility seems to be not realistic: once a CH_3 group in a saturated hydrocarbon is oxidised, the second CH_3 group should undergo oxidation on the same catalyst even more easily, and the process would not stop at the required stage. On the other hand, dehydrogenation proceeds via the hydrogen atom(s) abstraction, but the H atom in the carbonyl group is the most weakly bound in the molecule that would form in the first stage. This would further decrease the probability of the sequential formation of acrolein.

Up to now there are also no reliable data in the literature indicating that acrolein could form from propane via the simultaneous dehydrogenation and oxygen insertion. Such a process would require (a) the presence on the surface of active sites of complex configuration carrying two functions simultaneously, and (b) specific chemisorption of a propane molecule providing an efficient attack of two different parts of it by different "functional tools" of the complex active site. The latter requirement is nearly beyond the accessible limits, if one takes into account all the surface chemistry of light paraffins known to date.

As to the sequential formation of acrolein via ODH of propane and POA of propene, both parts of this process are well-known in the literature, numerous catalysts have been developed and some of them are used in practice. 25–27% propene yield in propane ODH and >85% acrolein yield in POA of propene can be achieved [1–4]. By combining the above stages in two sequential reactors, one could achieve up to 25% acrolein yield. Unfortunately, a big gap does exist between the optimal conditions required for the two macro-stages: the most efficient propane ODH proceeds at elevated temperatures ($>500\,^\circ$C), short residence times (<0.1 s), and high propane-to-oxygen ratios; in contrast, propene POA over the most efficient catalysts requires relatively low temperatures (<400 °C), long residence times (several seconds) and excess of oxygen in the feed.

We have undertaken this study in order to see if the two functions discussed above could be coupled in one single reaction space, and whether or not active sites for these two macro-steps would interfere. The model catalytic system for propane POA consisted of two catalysts, each of them displaying a high efficiency in one of the two separate processes: $VSbBiBa/Al_2O_3$ (further denoted as Cat.1) for propane ODH and MoBiCoFe complex oxide (Cat.2) for propene POA, respectively.

2. Experimental

The catalysts were used in two different modes: individually and combined. In the latter case three different configurations of the catalyst bed were utilized: (a) *separate layers:* two catalysts placed into the reactor in one layer after another along the direction of the gas flow; (b) *rough (mechanical) mixture:* mixture of Cat.1 spheres (size 0.3–0.8 mm) and Cat.2 grains (1.0–2.0 mm); (c) *fine (intraparticular) mixture:* mixed particles (of 0.3–0.8 mm size) prepared from a mechanical mixture of the two catalysts finely ground separately. In a typical experiment 0.6 g of Cat.1 and 0.2 g of Cat.2 were combined. Cat.1 ($VSbBiBa/\gamma\text{-}Al_2O_3$) and Cat.2 (MoBiCoFe complex oxide) were prepared by impregnation and by co-precipitation, respectively.

Catalytic experiments were carried out in a flow-type fixed-bed tubular quartz reactor (i.d. 6 mm) equipped with a chromel–alumel thermocouple placed into a quartz cover and inserted into the catalyst bed. The gas mixture was analyzed by an on-line GC system. Conversion of reactants (X), product selectivity (S) and yield (Y) are expressed as mol% and calculated on a carbon atom basis.

3. Results and discussion

The main experimental observations regarding the reactivities of propane, propene and acrolein over individual catalysts below 500 °C may be summarized as follows:

(1) Propane can be transformed into propene over Cat.1; the efficiency of this process increases at higher temperatures (see table 1); no oxygenate formation is observed.

(2) Propane reactivity over Cat.2 is very low; in this case almost only total oxidation takes place.

(3) Reactivity of propene over Cat.1 is higher than that of propane causing a limited efficiency of the ODH process; carbon oxides are solely formed during the propene oxidation over Cat.1.

(4) Propene undergoes a highly efficient POA over Cat.2: at $\leqslant$300 °C and ~10 s contact times, $\geqslant$85% acrolein yield can be reached; carbon oxides and acids (acetic and acrylic) form as by-products.

Table 1
Propane ODH over Cat.1 (41.7 ml/min g, 10.3% C_3H_8+8.7% O_2 in He).

t (°C)	$X_{C_3H_8}$ (%)	X_{O_2} (%)	$S_{C_3H_6}$ (%)	$Y_{C_3H_6}$ (%)
360	23.6	100	11.1	2.6
380	24.5	100	11.9	2.9
400	24.75	100	16.5	4.1
420	25.3	100	19.2	4.85
440	25.8	100	21.9	5.6

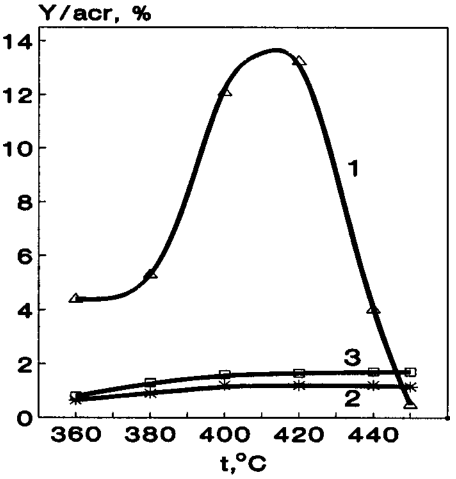

Figure 1. Acrolein yield vs. temperature ($W = 25$ ml/min): (1) separate layers, (2) rough mixture and (3) fine mixture.

(5) Acrolein reactivity over Cat.2 is relatively low as compared to that of propene below 440 °C; the difference in their reactivities gradually decreases at rising temperature.

(6) Acrolein is highly reactive over Cat.1 producing total oxidation products.

When both Cat.1 and Cat.2 are placed into the reactor, all the trends of the process are significantly different from those observed over separate catalysts and strongly affected by the layer configuration. Figures 1 and 2 show the trends in acrolein yields at varying temperature and total flow rate. Propene yields are comparable over different configurations of the catalyst bed, but follow different trends. While over mixed layers it passes through flat maxima when varying flow rate, in the case of separate layers the sharp minimum in propene yield is observed. This minimum coincides with the peak acrolein formation. The following jump in propene yield (and dropping acrolein yield) corresponds to the conditions at which almost total oxygen conversion takes place.

As mentioned in [1,3], maximal acrolein yields from propane were achieved in [5] under conditions where primary gas-phase propane dehydrogenation occurred, i.e., acrolein is likely to form via the initially formed propene oxidation. In order to see if the same should be applicable to our experiments, let us compare the behaviour of

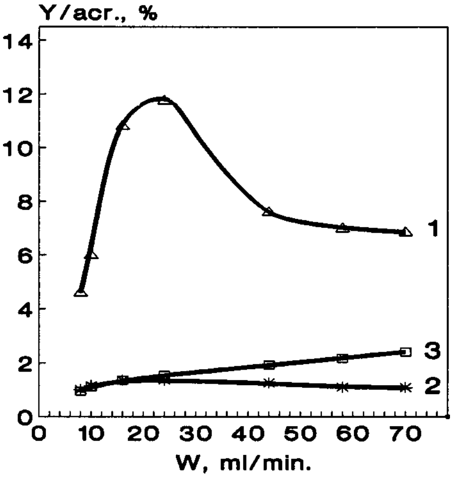

Figure 2. Acrolein yield vs. total flow rate ($t = 400\,^{\circ}$C): (1) separate layers, (2) rough mixture and (3) fine mixture.

Table 2
Propane oxidation over combined catalyst layers of different configurations (400 °C, 0.6 g Cat.1, 0.2 g Cat.2, 20 ml/min of 10% C_3H_8 + 10% O_2 in He).

Configuration	Conversion (%)		Selectivity (%)		Yield (%)	
	C_3H_8	O_2	C_3H_6	Acrolein	C_3H_6	Acrolein
Separate layers	18	85	10.5	62.8	1.9	11.3
Rough mixture	13.5	65	16.3	10.0	2.2	1.35
Fine mixture	11.5	50	22.6	12.2	2.6	1.4
2CR model (estimated)	24.5	>95	4.8	13.3	1.15	2.8

the combined layers arrangements with that of an imaginary model of two consecutive reactors (2CR) operated at the same temperature: the first one, containing Cat.1, is fed with a C_3H_8–O_2 mixture, and the second one, filled with Cat.2, fed with the products formed in the first one. The results (table 2) show that neither product selectivities, nor overall conversions are simple combinations of two consecutive processes. The total yield of partial oxidation products (propene + acrolein) over mixed layers is close to the additive one ("2CR model"), but with a predominance of propene. Over separate layers the dominant acrolein formation is even more pronounced than in the 2CR model. According to table 1, under the given conditions the propene yield in the first reactor cannot exceed 6%, which corresponds to <0.6 vol% at the exit. If we exclude the formation of carbon oxides in the post-catalytic volume, the concentration of unreacted oxygen could reach 5 vol% [6]. In these conditions an acrolein yield from propene of 64% could be achieved; thus the maximum accessible yield of acrolein from propane using the two consecutive reactors cannot exceed 4%. However, an experimental yield of 11.3% is obtained over a catalytic bed with separate, consecutive layers of Cat.1 and Cat.2. One may thus conclude that the scheme consisting of two sequential ODH and POA processes is not adequate to describe the process over combined layers. Conversion and selectivity patterns suggest that propane activation over Cat.1 leads to a formation of some intermediate, which reacts further giving final products. Transformations of this intermediate over Cat.1 would lead to propene and, likely, to total oxidation products. Over Cat.2 it would transform into acrolein, even more efficiently than propene would.

This assumed intermediate must be able to easily leave the layer of Cat.1, and it is a relatively short-living species to be not detectable by GC. The most probable candidate for the role of this intermediate is a gas-phase C_3H_7 radical. Indeed, the abstraction of a H atom from the propane molecule by a strong oxidative site on the Cat.1 surface is the most feasible process for the initial activation of propane [7]. The second H atom can be easily abstracted from the C_3H_7 radical either over Cat.1 or in the gas phase with the formation of propene. Also, total oxidation via consecutive reactions of C_3H_7 radicals, both in the gas phase and on the Cat.1 surface, is highly probable. So, the existing data on the properties of C_3H_7 radicals are consistent with those of the assumed intermediate claimed above.

As to the possible reactivity of (iso)propyl radicals over Cat.2, one may suggest that being captured by the surface sites, they are able to loose one by one two H atoms, forming an allylic (π- or σ-type) intermediate or any other precursor of acrolein. In this case the rate of acrolein formation could be higher than the one accessible in a conventional propene POA.

Over mixed layers a reduced propane conversion is accompanied by a relatively low selectivity to acrolein. In this case acrolein forms in the layer containing the catalyst able to conduct its rapid total oxidation (i.e., Cat.1 – see observation (6) above). If we assume the redox mechanism for propane ODH over Cat.1, the active sites of this catalyst would be actively reduced by acrolein. As a result, the rate of primary reaction of propane decreases along with acrolein selectivity.

The sequence of steps proposed above presumably proceeds in different "reaction zones": the formation of a highly reactive intermediate from the initial relatively inactive propane molecule proceeds in the "zone of high reactivity" and the much more reactive desired product (acrolein) forms in the "zone of low reactivity/high selectivity". Due to this spatial separation one is able to preserve it from sequential transformations and to achieve elevated selectivities at moderate conversions. It is evident, however, that a process of such a complex character requires additional studies for its more detailed description. Nevertheless, one may assume that, if the mechanism proposed above is correct in general outline, it could be used as a guideline for the further development and optimisation of the process.

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