

# Elucidation of the reactivity of different oxygen species over V-Ti-O surface towards partial oxidation of light hydrocarbon using isotope methods

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## Introduction

Vanadia is one of the most efficient catalysts for partial oxidation of hydrocarbons. Despite the numerous studies dealing with investigation of kinetics and mechanisms of this reaction, the main question – what are the factors determining the selectivity – remains unanswered. Nowadays the subject of wide speculation is the role played by the different surface oxygen species in governing the reaction towards partial or complete oxidation, including the most debatable question concerning the participation of hydrated VOH species in partial oxidation [1]. In this work using isotope exchange with H<sub>2</sub><sup>18</sup>O we succeeded in maintaining the non-equilibrium distribution of <sup>16</sup>O and <sup>18</sup>O in hydrated and dehydrated active sites, which enabled us to show that it is VOH species that take part in the formation of the desired product of 1-butene oxidation – acetic acid.

## Experimental

The isotope kinetic study of 1-butene oxidation over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and oxygen exchange between catalyst, dioxygen and water was performed at close conditions: plug-flow reactor, atmospheric pressure, temperature range of 160-280°C. Following types of isotopic experiments were carried out: a) the switches <sup>18</sup>O<sub>2</sub>/<sup>16</sup>O<sub>2</sub> in O<sub>2</sub>(+H<sub>2</sub>O)+He and C<sub>4</sub>H<sub>8</sub>+O<sub>2</sub>(+H<sub>2</sub>O)+He flows (SSITKA); b) H<sub>2</sub><sup>18</sup>O addition into O<sub>2</sub>+He and C<sub>4</sub>H<sub>8</sub>+O+He flows.

## Results/Discussion

Study of oxygen exchange between vanadia, O<sub>2</sub> and H<sub>2</sub>O [2] showed that in the temperature range that is typical for the most reactions of partial oxidation (150-250°C) the rate of oxygen exchange (*W*) of H<sub>2</sub>O with VOH groups is more than two orders of magnitude higher than that with VO. So, at 220°C: *W*<sub>VO</sub> ≈ 10<sup>-3</sup> s<sup>-1</sup> (per one site) and *W*<sub>VOH</sub> ≈ 0.2 s<sup>-1</sup>. In comparison with water, the rate of dioxygen isotope exchange with vanadia is negligible.

Two competitive processes, i.e. isotope exchange with water (resulting in the enrichment of active sites by <sup>18</sup>O) and catalyst reoxidation by <sup>16</sup>O take place during oxidation of hydrocarbons

in the presence of H<sub>2</sub><sup>18</sup>O. <sup>18</sup>O isotope fractions in VOH and VO ( $\alpha_{\text{VOH}}$  and  $\alpha_{\text{VO}}$ , respectively) are determined by the ratio between the rate of oxygen exchange *W*<sub>VOH(VO)</sub> and that of the reaction over these sites *R*<sub>VOH(VO)</sub>. Provided the value of summarized rate of the reaction *R*<sub>VOH</sub>+*R*<sub>VO</sub> lies between *W*<sub>VOH</sub> and *W*<sub>VO</sub>, then  $\alpha_{\text{VOH}}$  and  $\alpha_{\text{VO}}$  will be substantially different:  $\alpha_{\text{VOH}} \gg \alpha_{\text{VO}}$ . In this case isotope composition of oxidation products depends on the type of active sites participating in their formation.

As can be seen from Fig. 1, H<sub>2</sub><sup>18</sup>O addition into the reaction mixture C<sub>4</sub>H<sub>8</sub>+O<sub>2</sub> resulted in the transfer of labeled oxygen to AcOH [3]. Numerical analysis of the dynamics of isotope transfer and distribution of differently labeled AcOH molecules showed that the hydrated centers exhibit high activity in partial oxidation of 1-butene in contrast to dehydrated VO centers, which favor total oxidation. So, the turnover frequency of 1-butene to AcOH over VOH centers is at least three times higher than over VO centers [4]. On addition of water steam to the reaction mixture the concentration of VOH centers increases resulting in the higher selectivity towards the main product.

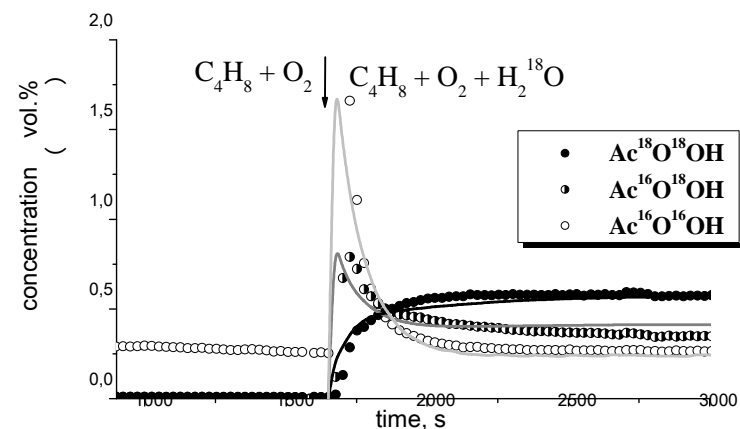


Figure 1. Modeling of transient regimes upon addition of H<sub>2</sub><sup>18</sup>O to the feed (points – experiment, lines – calculation). T=220°C.

## References

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