UNIVERSITEIT GENT

FACULTY OF **ENGINEERING AND ARCHITECTURE**

Design of a Novel VO_x/WO_x Catalyst for the Oxidative Dehydrogenation of Propane

Isabelle Ascoop†,*, Vladimir V. Galvita*, Guy B. Marin* and Pascal Van Der Voort†

†COMOC (Center for Ordered Materials Organometallics & Catalysis)

Krijgslaan 281 (S3), 9000 Ghent, Belgium
http://www.we06.ugent.be/comoc E-mail: isabelle.ascoop@UGent.be

***Laboratory for Chemical Technology**

Technologiepark 914, 9052 Ghent, Belgium
http://www.lct.UGent.be

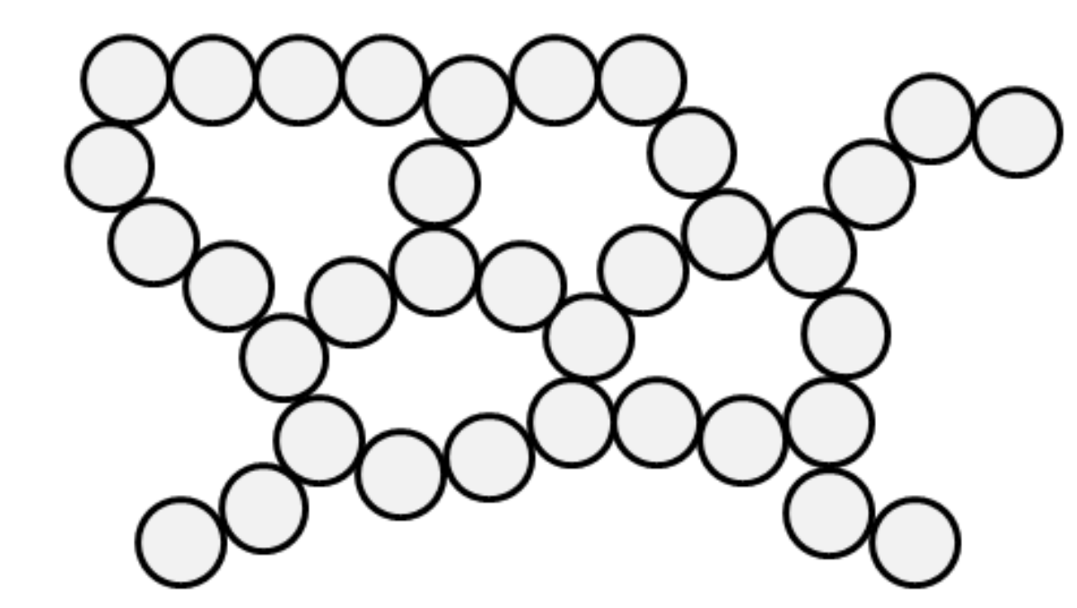
European Research Institute of Catalysis

Introduction

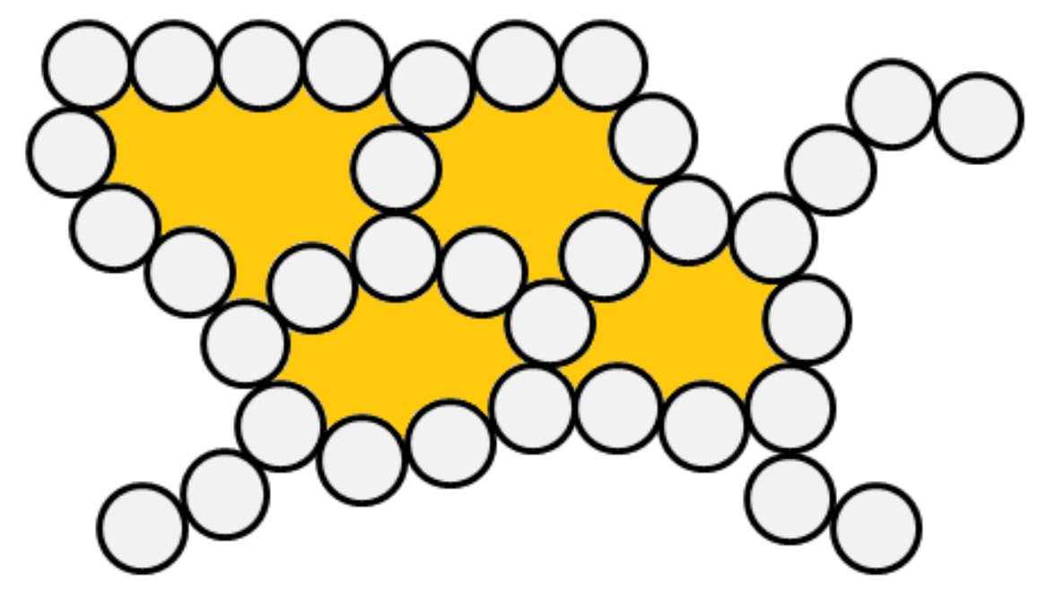
The Oxidative Dehydrogenation (ODH) process has great potential to provide an answer to the increasing propylene consumption.
ODH is the most attractive selective alkane converting processes due to its exothermic characteristic and the lack of thermodynamic limitations in comparison with steam cracking, fluid catalytic cracking and catalytic dehydrogenation.

Until now a trial design of a vanadium-tungsten oxide impregnated in silicagel has been synthesized and tested on its catalytic activity and selectivity. This type of catalyst is a testcase for the future development of mesoporous titania supported VO_x/WO_x catalysts.

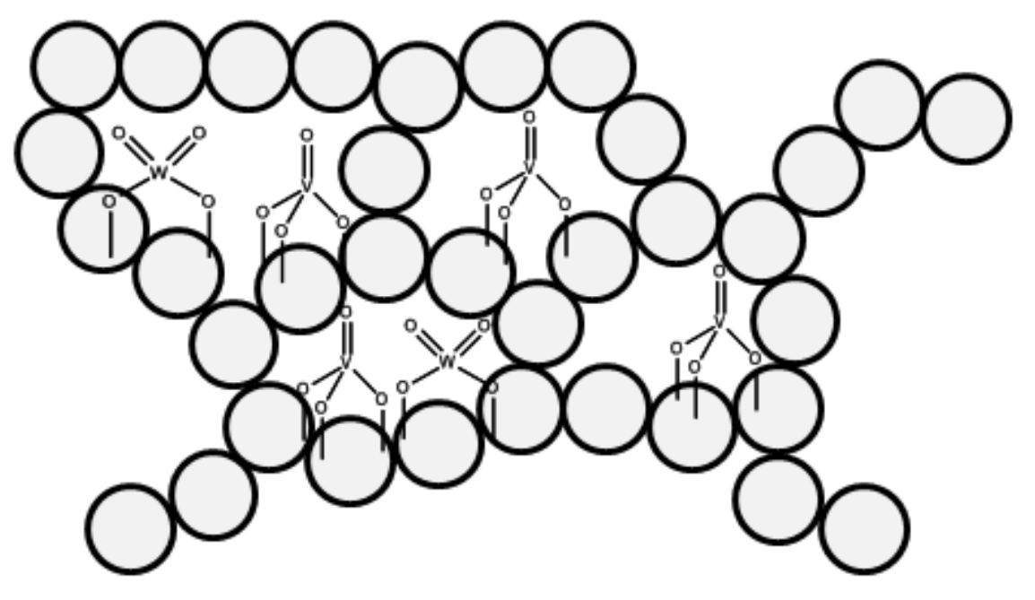
Synthesis, Characterization & Catalysis



Kieselgel 60 (= silicagel) is impregnated via incipient wetness (= dry impregnation method) with a aqueous solution of ammoniummetavanadate and ammonium tungstate.



Impregnated silica powder is calcined at 500°C with a heating rate of 2°C/min. for 6 hours.



Depending on the impregnated solution a VO_x or VO_x/WO_x functionalised kieselgel 60 is obtained (see Table 1 for the composition).

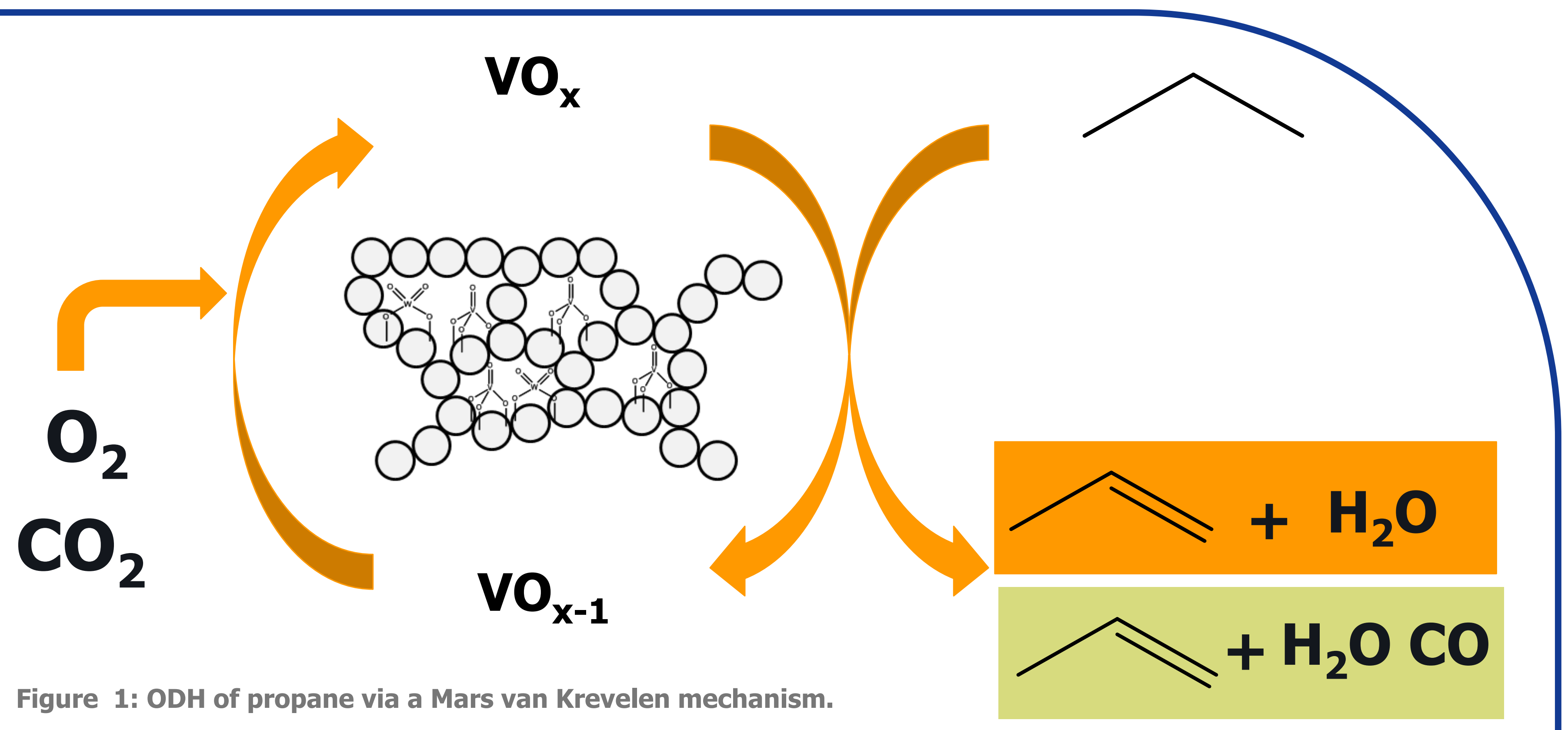
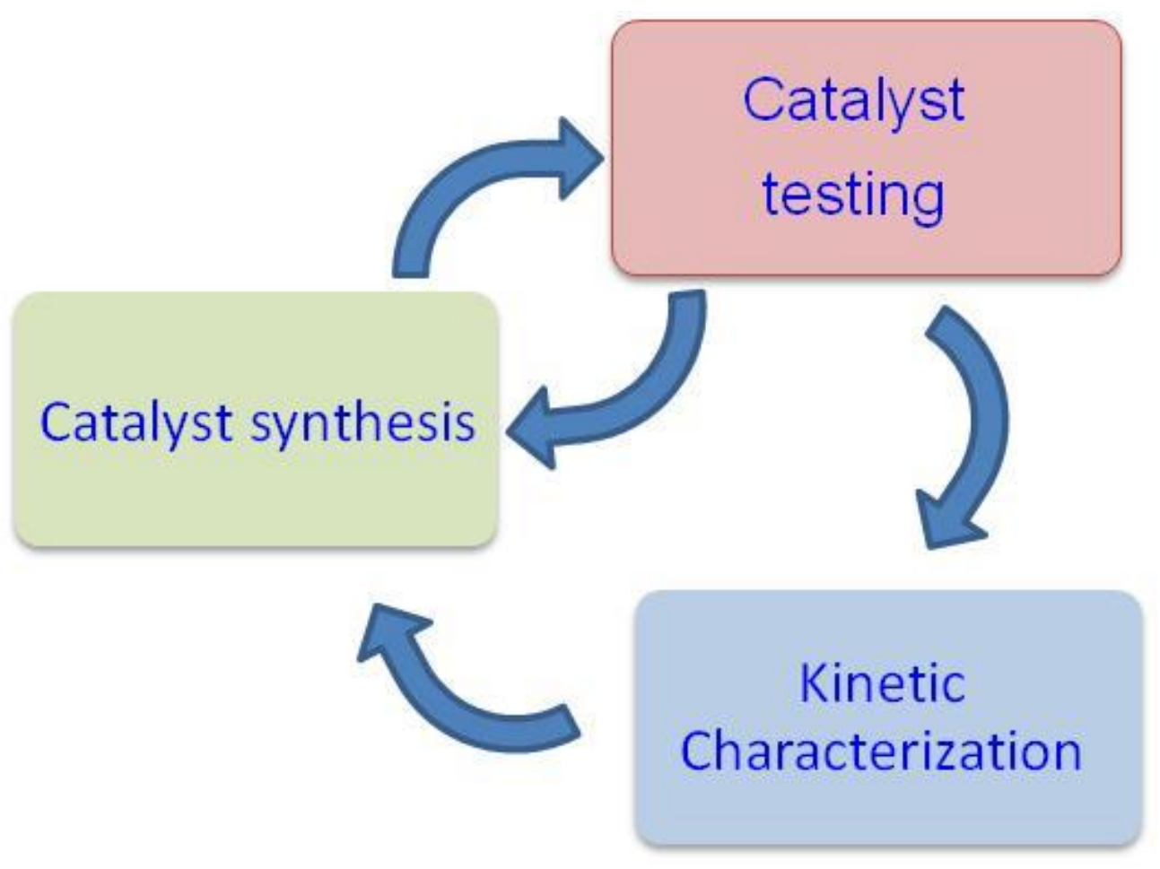


Figure 1: ODH of propane via a Mars van Krevelen mechanism.

ODH of propane will occur via a Mars van Krevelen mechanism



Sample	ICP analysis vanadium		ICP analysis tungsten	
1	3,2 w%	0,63 mmol/g		
2	5,7 w%	1,12 mmol/g		
3	3,4 w%	0,65 mmol/g	1,5 w%	0,08 mmol/g
4	4,1 w%	0,80 mmol/g	4,5 w%	0,25 mmol/g
5	3,3 w%	0,65 mmol/g	6,8 w%	0,37 mmol/g

Table 1: ICP results of synthesized VO_x and VO_x/WO_x catalysts.

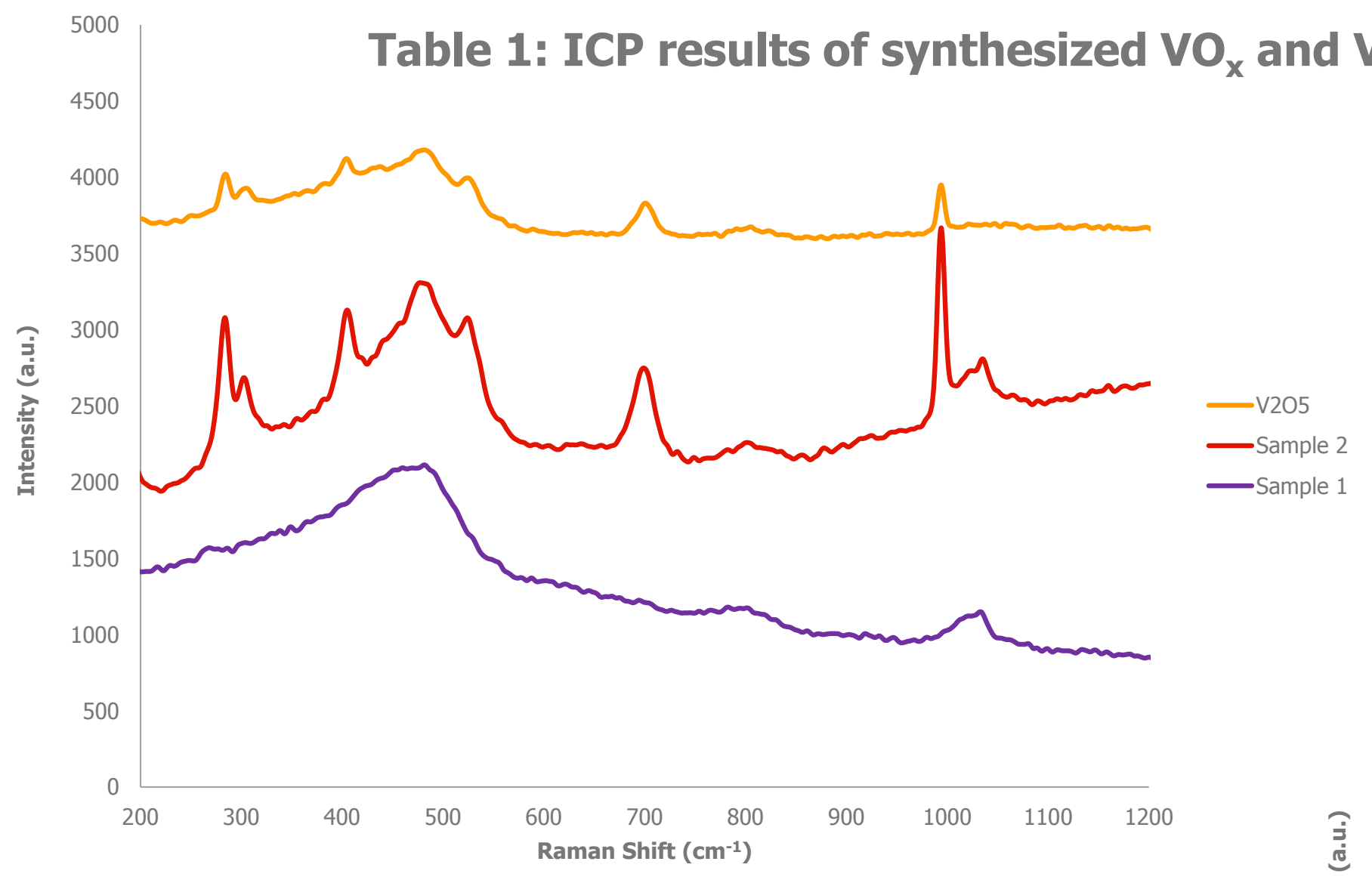


Figure 2: Raman spectra of VO_x impregnated samples.

Figure 2 shows that V_2O_5 cluster formation starts at 5,7 w% of vanadium.

Addition of WO_x hinders the formation of V_2O_5 clusters for the same impregnated concentration. Figure 3 shows no V_2O_5 vibrations.

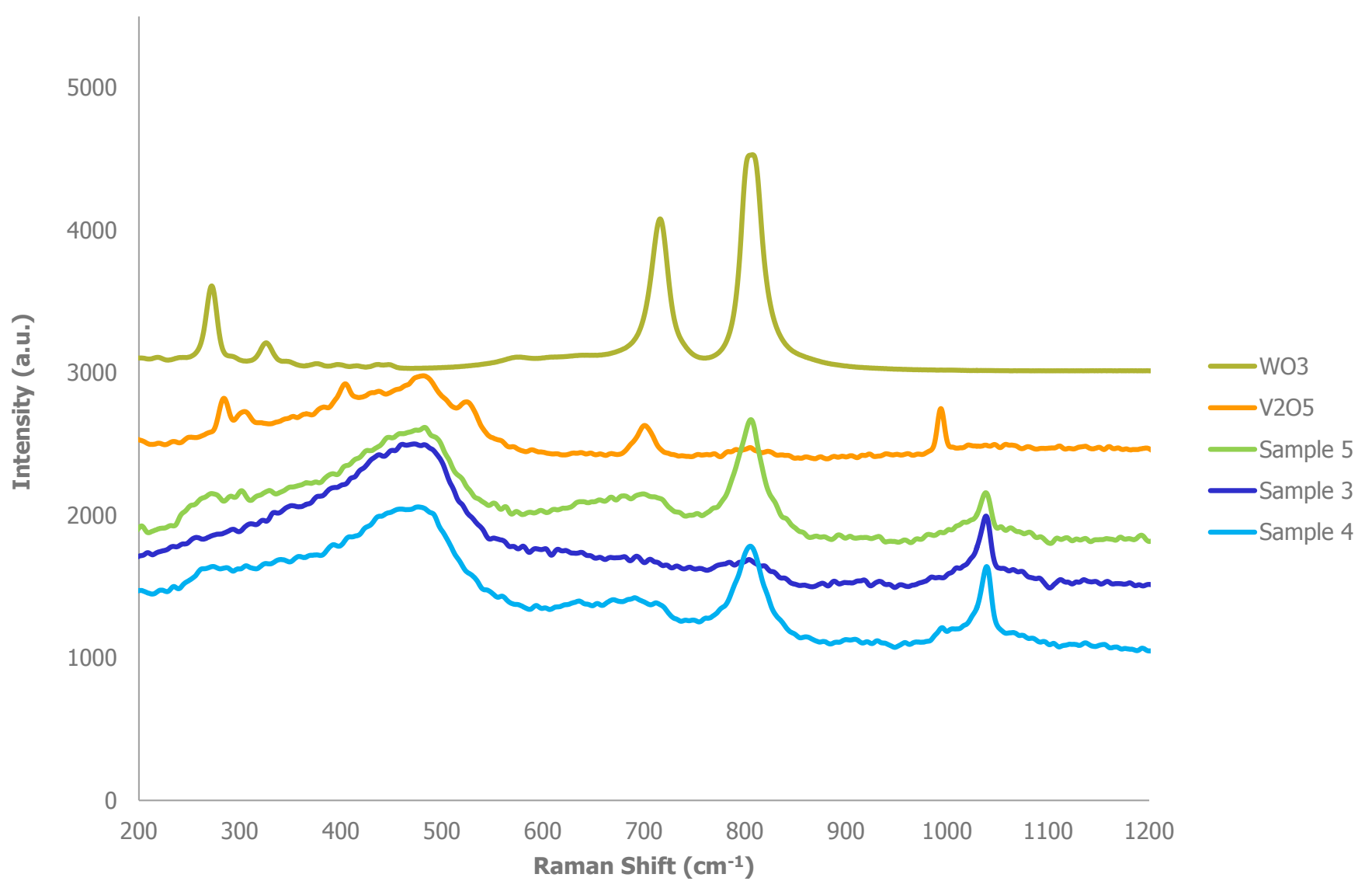


Figure 3: Raman spectra of VO_x/WO_x impregnated samples.

Sample	Selectivity	Space Time Yield ($mol.s^{-1}.g^{-1}$)
2	4,28%	$2,74 . 10^{-6}$
3	5,49%	$2,23 . 10^{-6}$
4	7,16%	$3,05 . 10^{-6}$

Table 2: Selectivity and space time yield at 550°C, calculated by the use of TPR with a heating rate of 20°C/min.

The bulk V_2O_5 shows two distinctive peaks in the H_2-TPR, due to respectively the terminal and apical oxygens. Although the highly loaded VO_x on silica catalyst, 5,7w% of vanadium, show clearly the formation of V_2O_5 crystallites in Raman, this is not reflected in the TPR profile (see Figure 4).

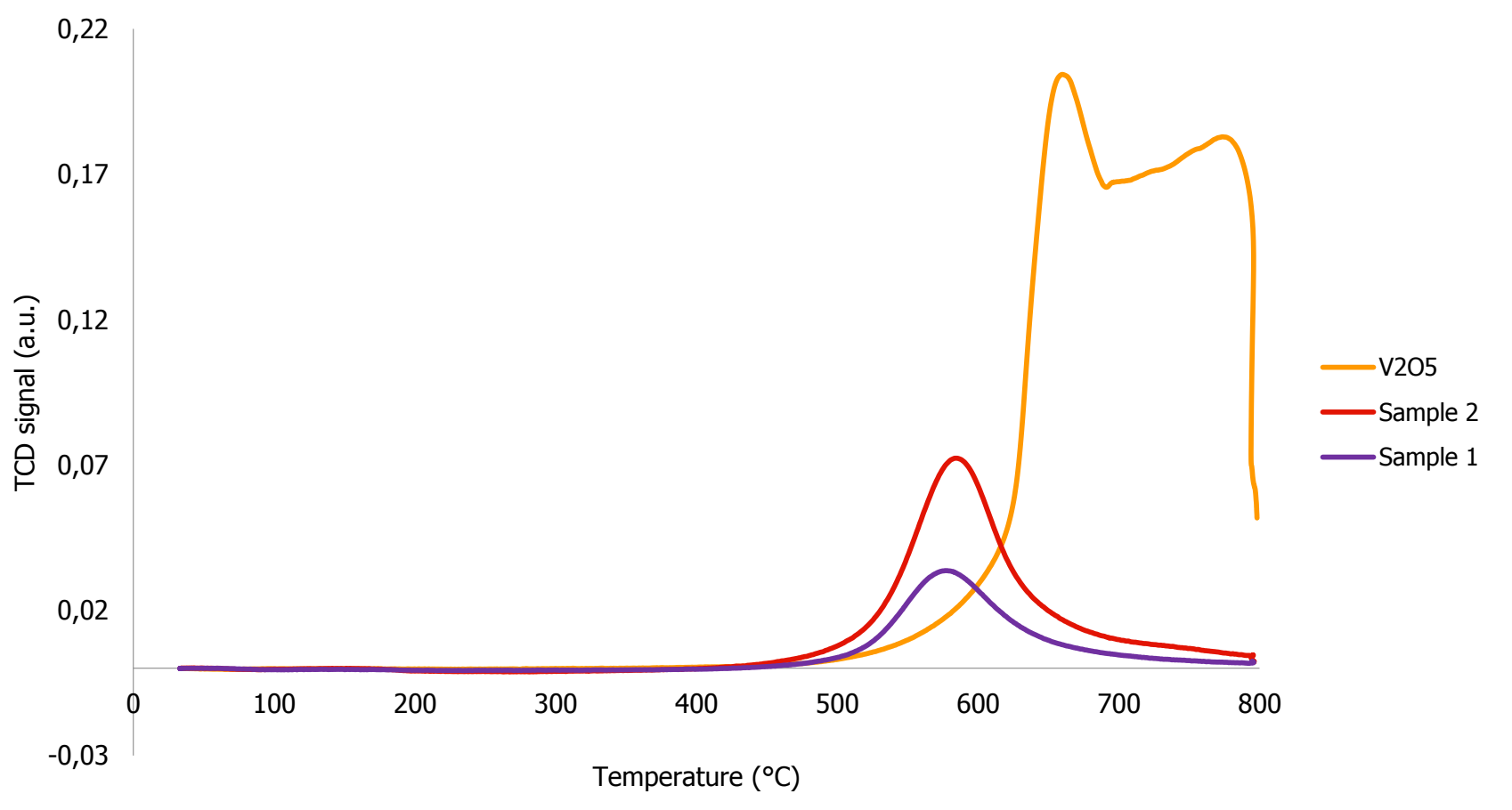


Figure 4: H_2-TPR of VO_x impregnated samples.

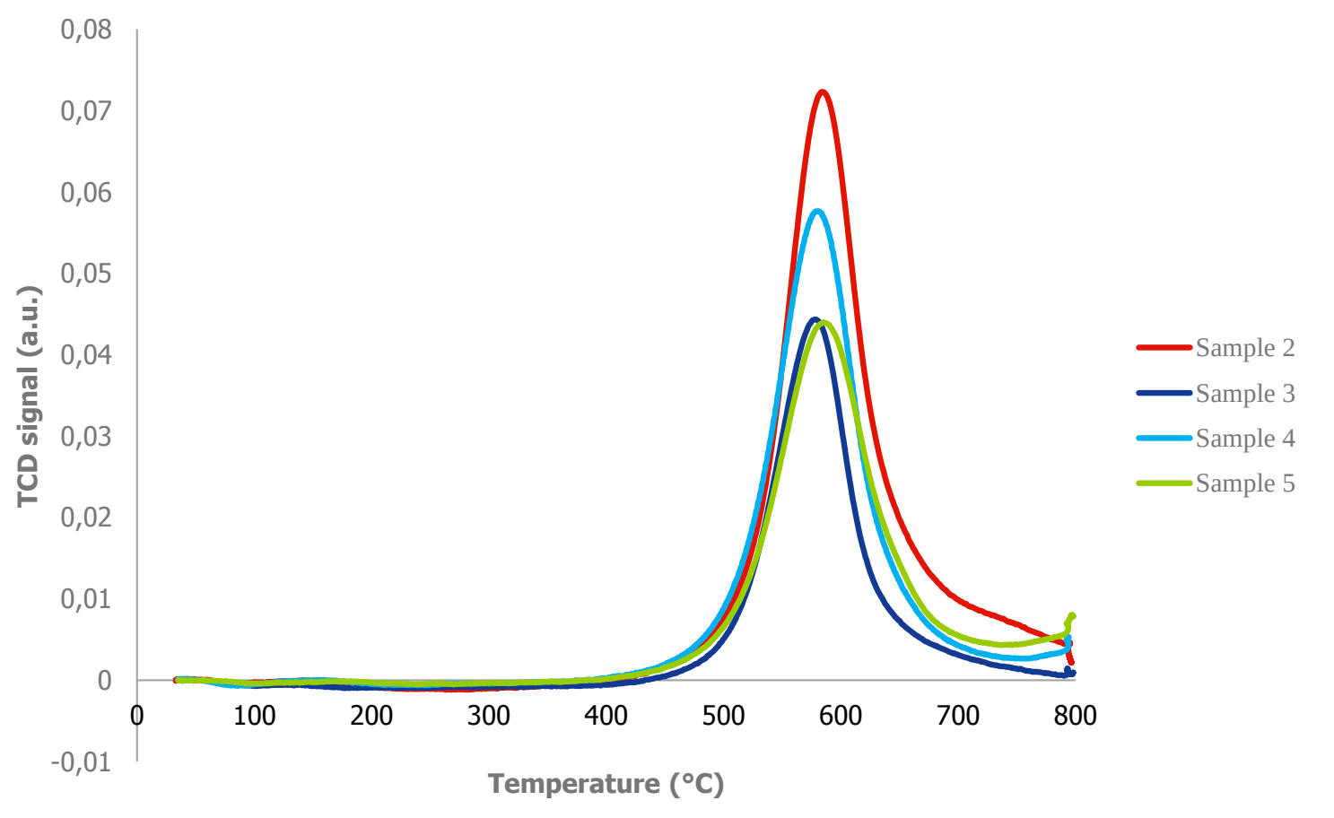


Figure 5: H_2-TPR of VO_x/WO_x impregnated samples.

Addition of WO_x to VO_x does not infuence the T_{max} and the presence of WO_x has no effect on the reactivity of the VO_x sites during H_2-TPR (Figure 5). Although there is no change in T_{max}, the precence of tungsten does increase the selectivity towards propylene (see Table 2) and thus the overall yield.

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