



# A microcalorimetric study of the adsorption of propane on MoVTeNb oxide

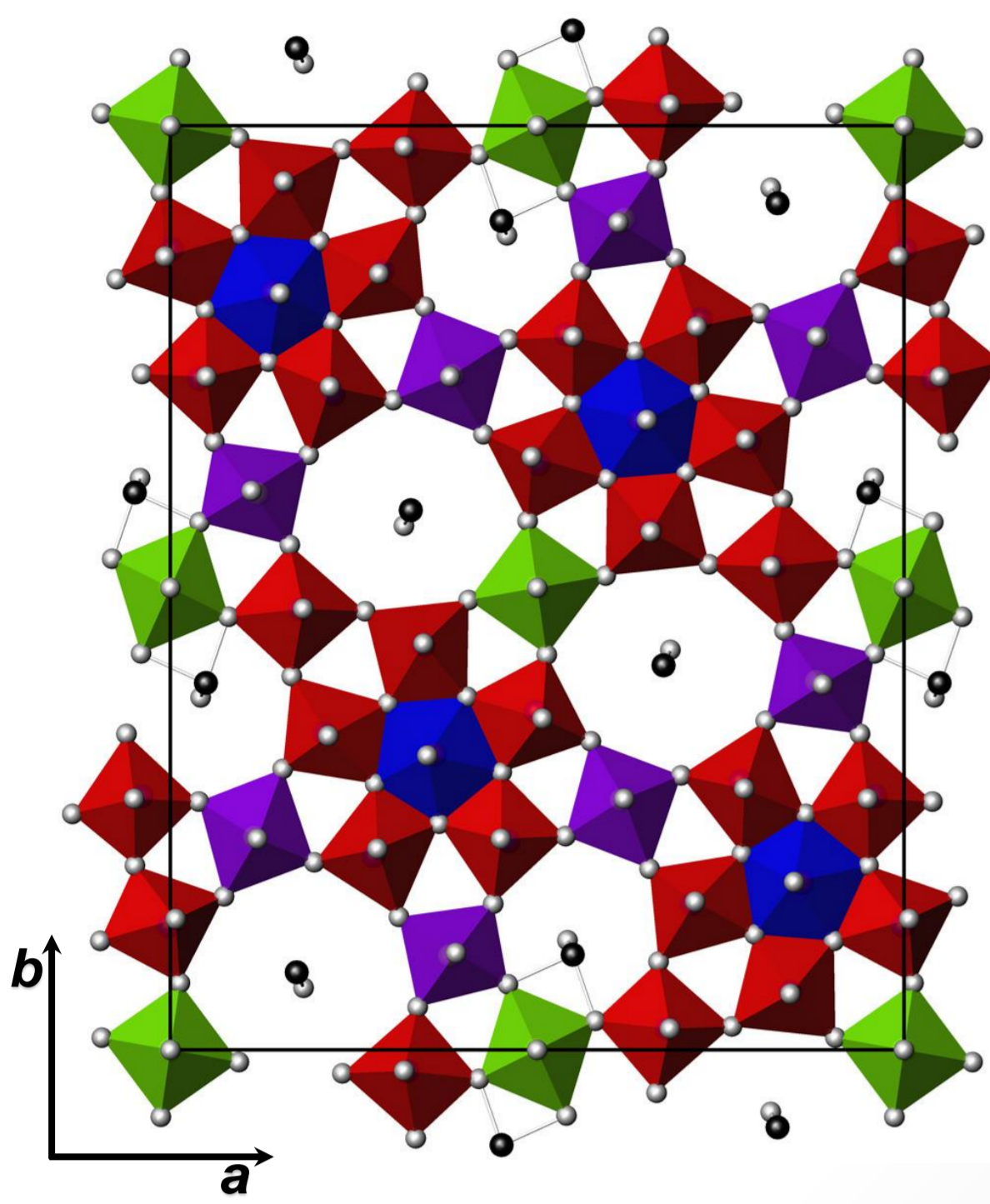


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## Introduction

Polycrystalline, mixed MoVTeNb oxides have been reported to show high selectivity and activity in direct oxidation of propane to acrylic acid. The most relevant crystal structure in C-H activation of propane is the orthorhombic, bronze-like  $\text{Mo}_{7.8}\text{V}_{1.2}\text{Te}_{0.937}\text{NbO}_{28.9}$  M1 phase [1]. Hydrogen abstraction and formation of propylene in the first step have been attributed to isolated vanadium sites located on terminating lattice planes (octahedra marked by violet colour). In the present work, the adsorption of propane on the surface of M1 has been studied by microcalorimetry. For this purpose, a series of highly crystalline, phase-pure M1 catalysts has been synthesized. The investigation is aimed at a deeper understanding of the mechanism of propane activation.



Schematic [001] view of M1 compound

## Conclusions

The number of propane adsorption sites (per  $\text{m}^2$ ) as well as the strengths of interaction of propane largely increases for the phase-pure M1 catalysts in comparison with its bare simple oxide components  
→ a new quality of the solid has been achieved via compositional and structural complexity of M1 catalyst  
The interaction of propane with the M1 catalysts at 313 K is reasonably weak and fully reversible.  
Adsorption of propane and nitrogen on M1 catalysts provide comparable surface area data.  
M1 catalysts show an propane adsorption order "n" higher than 1, reflecting an activated adsorption process, while its simple oxide bare components were established to be rather inactive over propane (n = 1).  
The most selective M1-a catalyst is characterized by  
(i) markedly higher initial differential adsorption heat of propane (71 kJ/mol) and  
(ii) highest value for the adsorption order n = 1.15, most likely owing to activated adsorption process.  
Microcalorimetric investigation suggests that tellurium play an important role in selectivity of M1 catalyst.

## Experimental

### Synthesis Method:

- M1 was prepared via three different methods:  
(i) hydrothermal synthesis → (catalyst M1-a),  
(ii) precipitation / spray-drying / purification → (catalyst M1-b) [2],  
(iii) superheated-water vapor treatment (SHWVT) → (catalyst M1-c) [3].

### Samples:

Catalyst (ID)	BET surface area [ $\text{m}^2/\text{g}$ ]	Mo:V:Te:Nb [at.-%]	Propane conversion [mol-%]	Selectivity to acrylic acid [mol-%]
M1-a (5511)	5.9	66 : 17 : 7 : 10	52	58
M1-b (6059)	8.8	62 : 17 : 7 : 14	55	43
M1-c (5737)	13.3	64 : 15 : 6 : 15	56	-

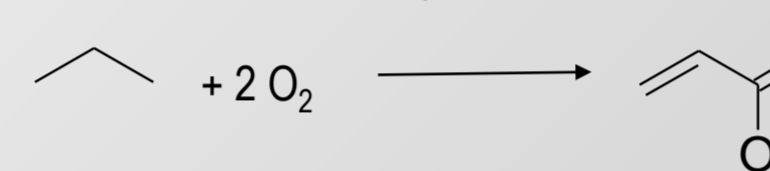
Reference bare components, mostly in highest oxidation state				
$\text{MoO}_3$ (6267)	1.8	100	-	-
$\text{V}_2\text{O}_5$ (7304)	3.2	100	-	-
$\text{Nb}_2\text{O}_5$ (7236)	42.0	100	-	-
$\text{TeO}_2$ (7604)	1.4	100	-	-

### Methods:

- Microcalorimeter SETARAM MS 70 with volumetric system [4, 5]  
→ The pressure-controlled dosing systems with calibrated volume allow measuring of the adsorbed amount (adsorption isotherm) simultaneously with differential heats of adsorption. Calorimetric sign criterion has been adopted, i.e. positive energetic quantity for an exothermic process.
- FTIR, PE100 spectrometer
- SEM, Hitachi S4800
- XRD, Bruker D8 ADVANCED diffractometer
- Standard multipoint BET analysis, Quantachrome Autosorb-6B analyzer

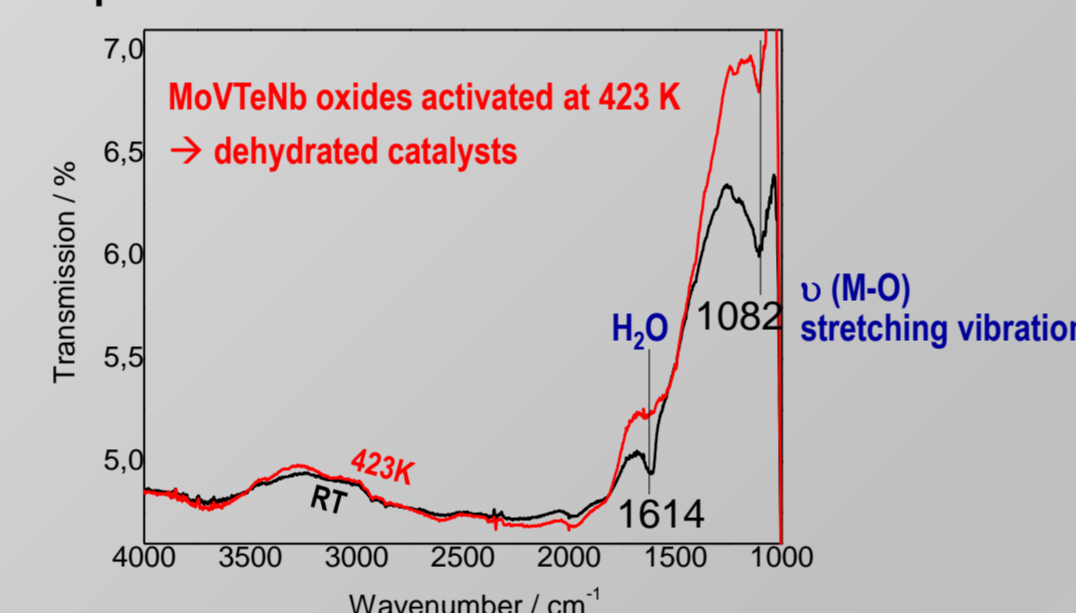
### Catalytic test in propane oxidation:

- Selective oxidation of propane to acrylic acid over M1  
Reaction conditions:  $T = 673 \text{ K}$ ,  $\text{GHSV} = 1200 \text{ h}^{-1}$   
 $\text{C}_3\text{H}_8/\text{H}_2\text{O}/\text{N}_2 = 3/6/40/51$  (vol.-%)

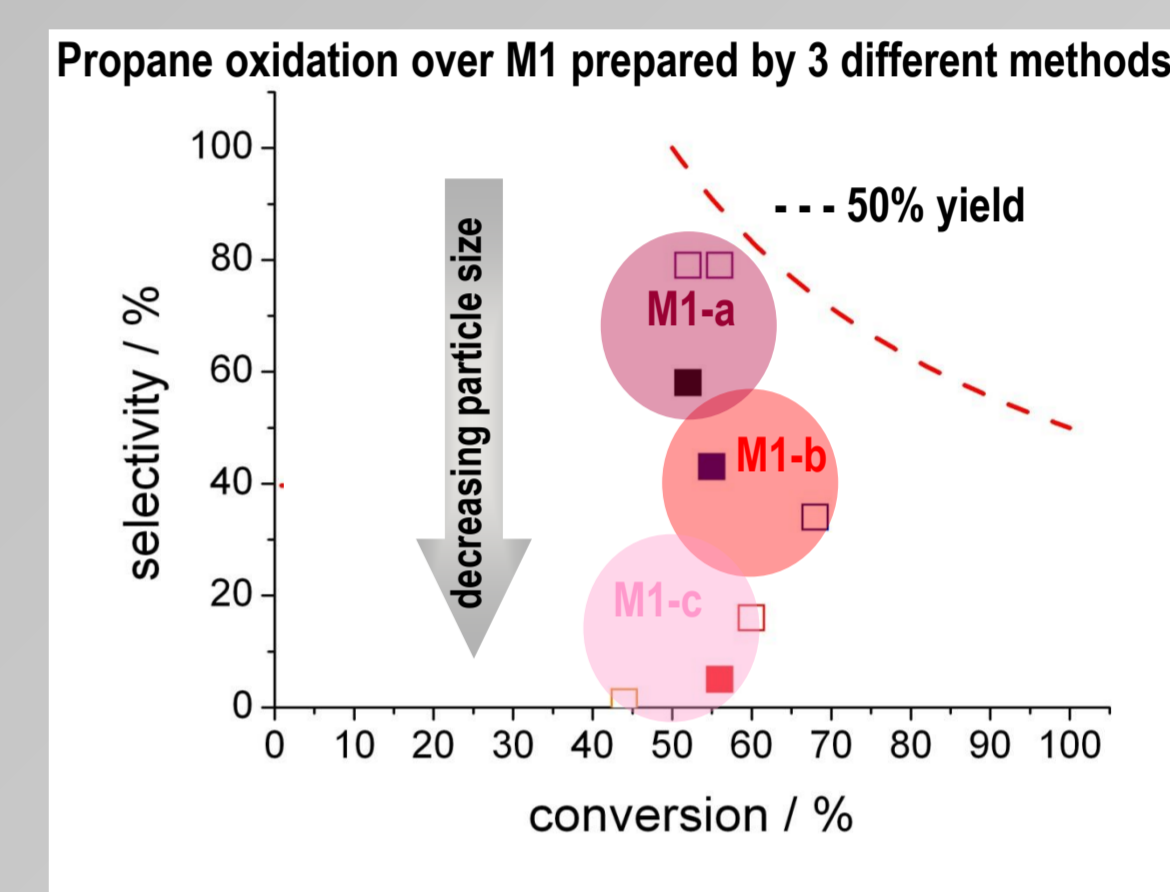
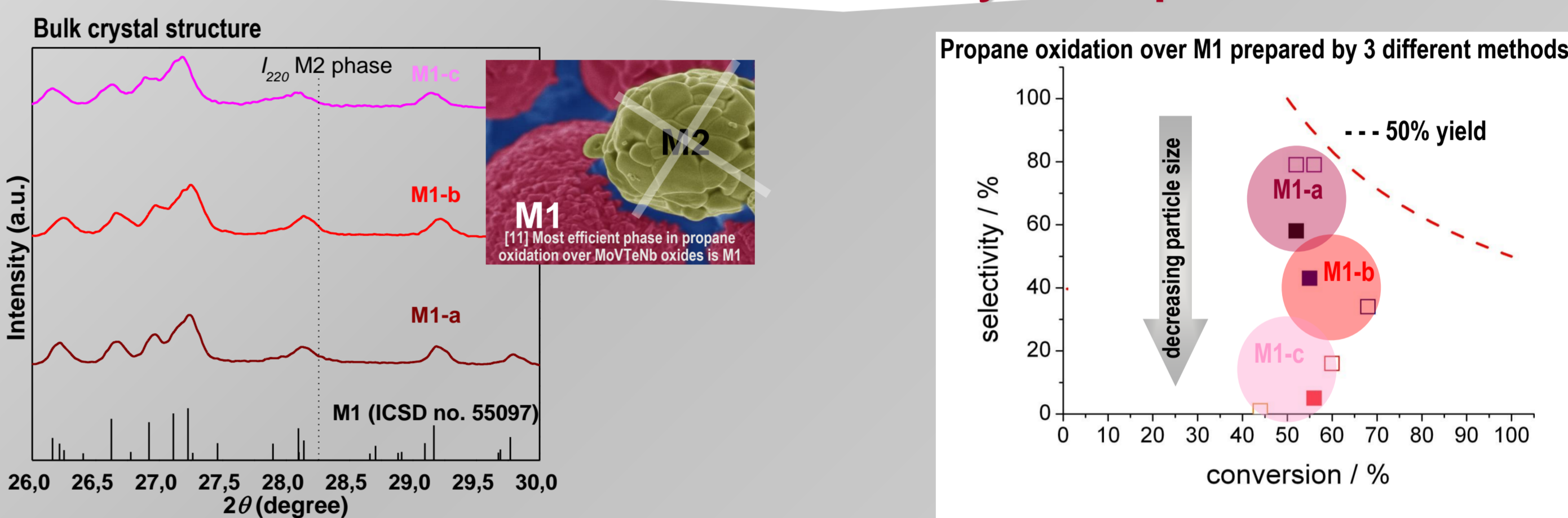


### Propane adsorption procedure at 313 K:

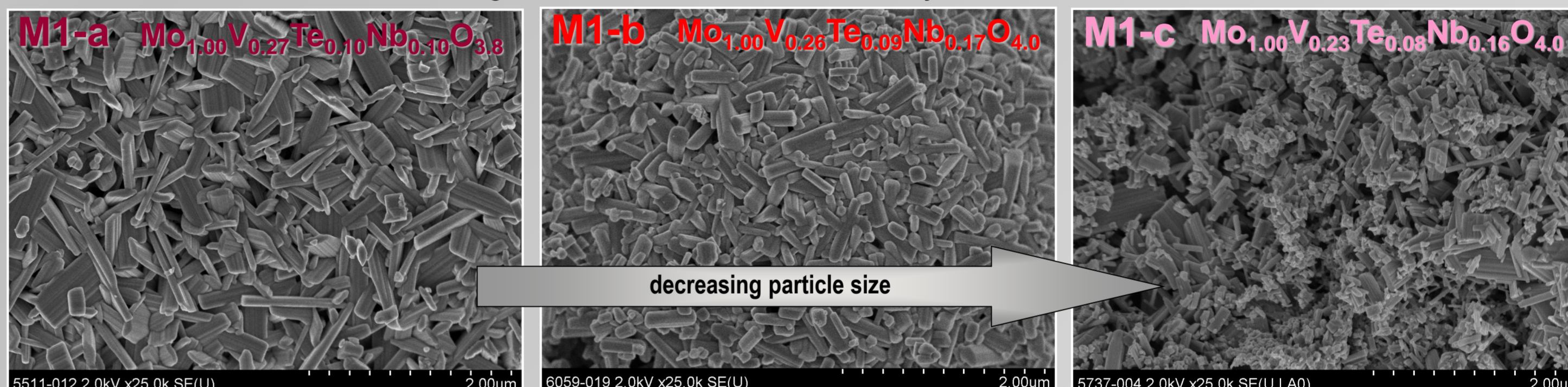
- Activation: mild activation conditions to minimize thermal and mechanical stress; samples were pressed at 123 MPa with following dehydration at 423 K under UHV for 1.5 h (final pressure  $10^{-6}$  mbar)
- Adsorption at  $T_{\text{ads}} = 313 \text{ K} < T_{\text{react}}$ , in order to prevent secondary reactions, and thus to investigate the pure adsorption enthalpy of propane
- Propane adsorption followed by desorption throughout evacuation, then re-adsorption of propane followed by desorption



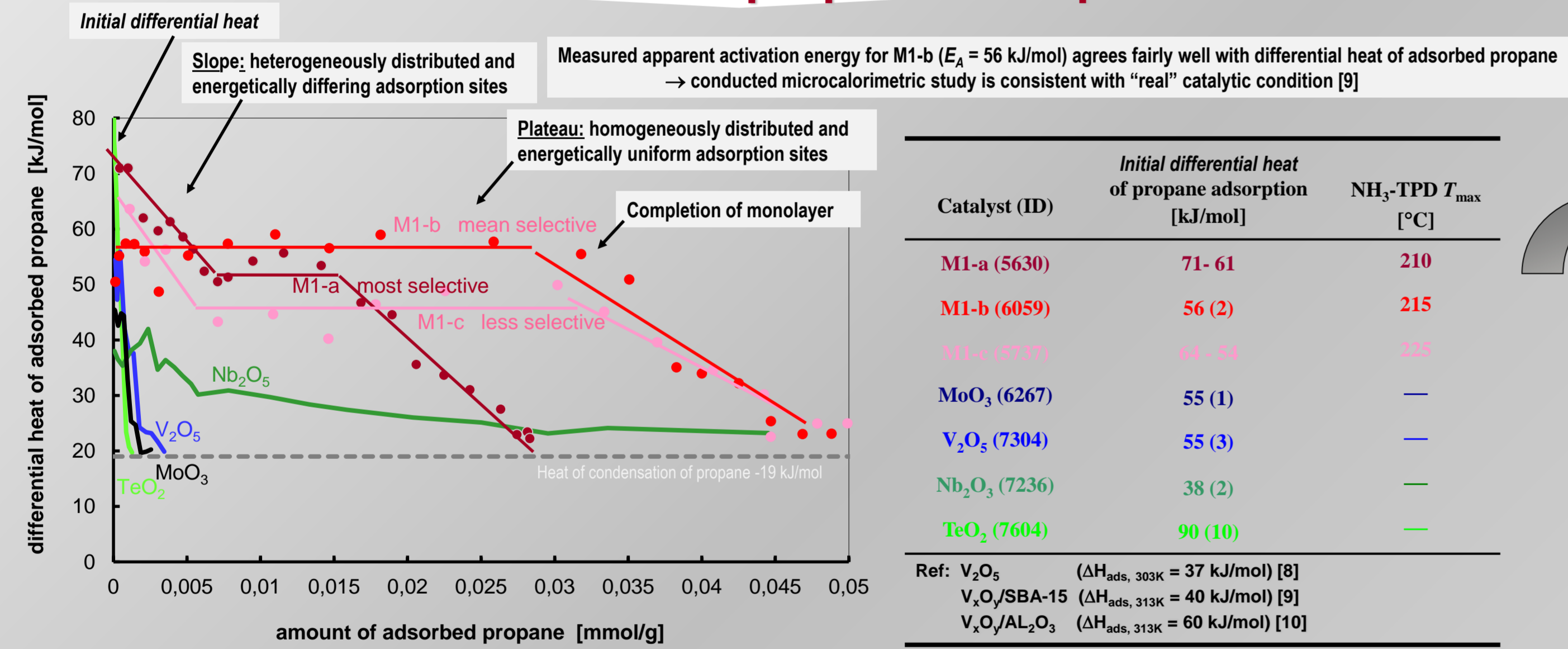
## Characteristics and Catalytic Properties



- Different preparation methods result in entirely phase-pure M1
- The particle size of single phase and highly crystalline M1 can be tailored by the preparation method
- Nanostructuring of M1 leads to the fall-off in selectivity



## Differential heat of propane adsorption

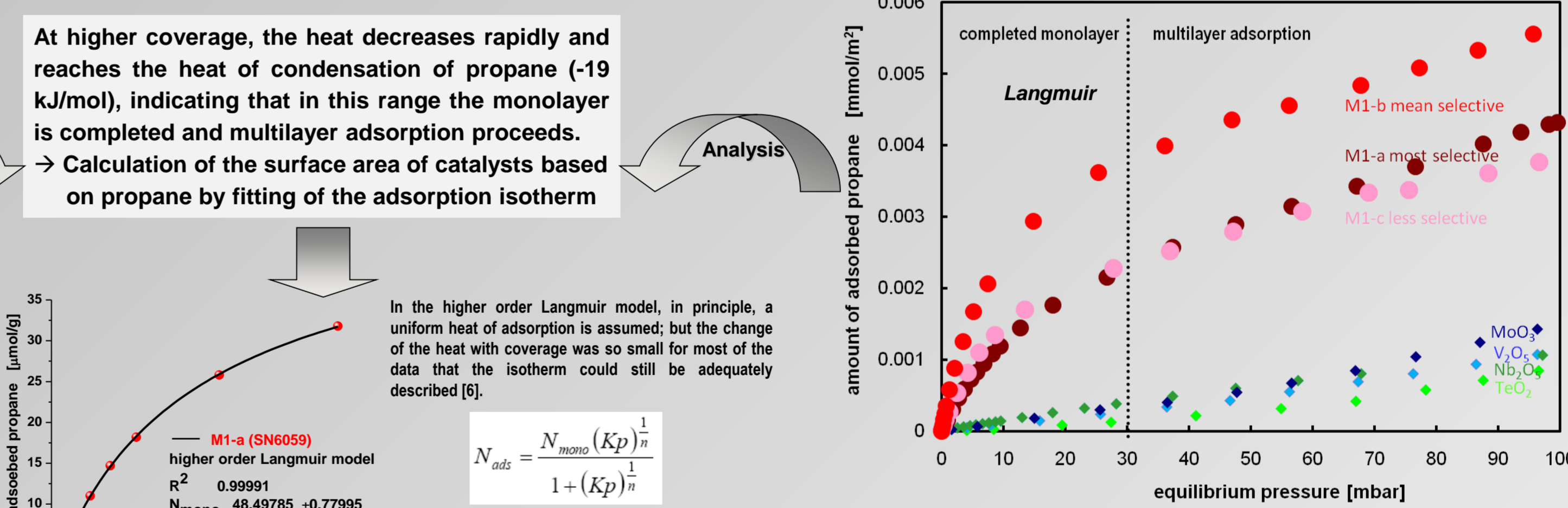


Catalyst (ID)	Initial differential heat of propane adsorption [kJ/mol]	$\text{NH}_3$ -TPD $T_{\text{max}}$ [°C]
M1-a (5630)	71-61	210
M1-b (6059)	56 (2)	215
M1-c (5737)	54 (3)	227
$\text{MoO}_3$ (6267)	55 (1)	-
$\text{V}_2\text{O}_5$ (7304)	55 (3)	-
$\text{Nb}_2\text{O}_5$ (7236)	38 (2)	-
$\text{TeO}_2$ (7604)	90 (10)	-

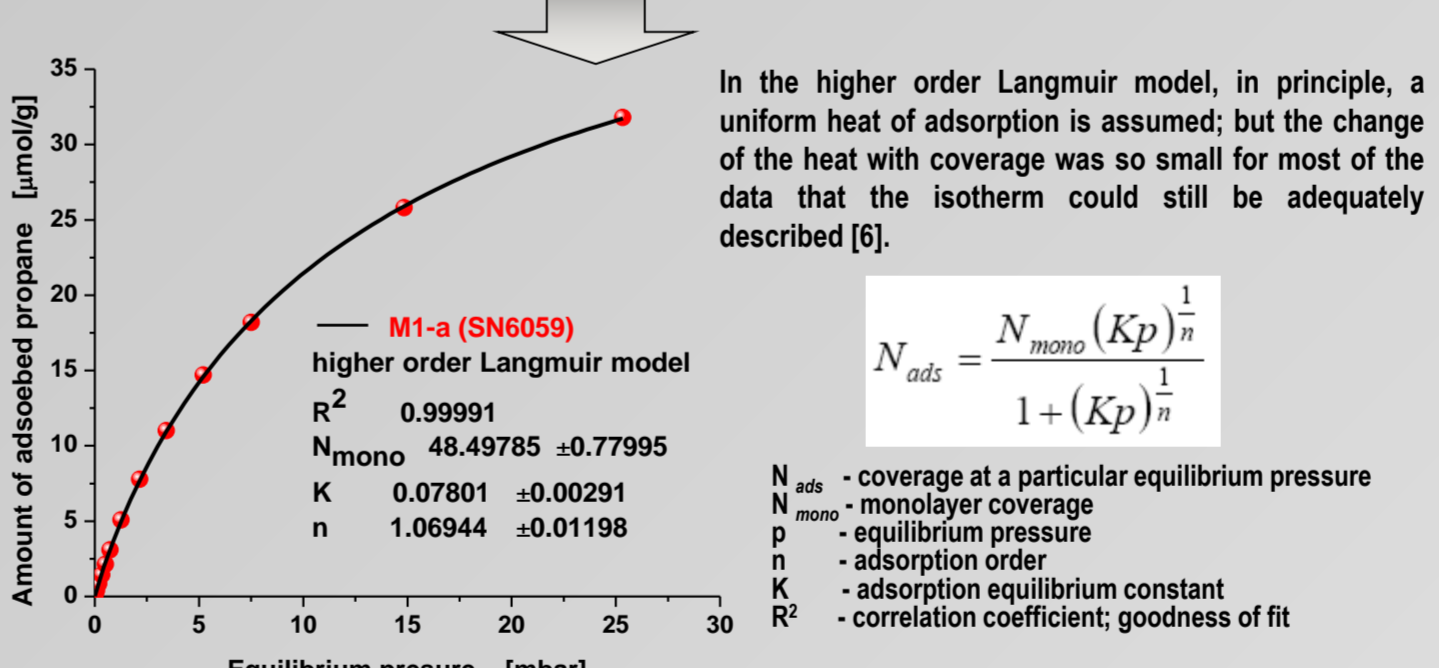
M1 - minority of energetically strong surface sites ≠ bare components: marginal amount of adsorption sites for propane with an extreme heterogeneous character

- The differential heat of propane markedly increases for M1 catalysts cf. its bare components  
→ a new quality of the solid has been achieved via compositional and structural complexity of M1 catalyst
- The most selective M1-a shows the highest initial differential heat cf. other M1 catalysts.  
Pure  $\text{TeO}_2$  exhibits the highest initial differential heat cf. other investigated bare components.  
→ Te seems to be essential for high selectivity taking into account observed minority of strong adsorption surface sites for propane.

## Propane adsorption isotherm



At higher coverage, the heat decreases rapidly and reaches the heat of condensation of propane (-19 kJ/mol), indicating that in this range the monolayer is completed and multilayer adsorption proceeds.  
→ Calculation of the surface area of catalysts based on propane by fitting of the adsorption isotherm



$$\text{Surface area}_{\text{propane}} = N_{\text{mono}} \cdot \text{cross-section area}_{\text{propane}} \cdot \text{Avogadro constant}$$

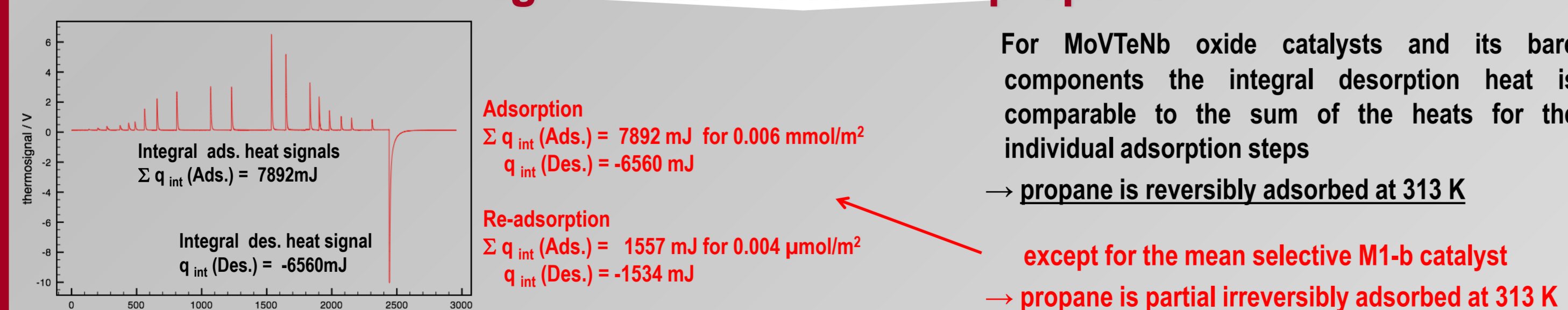
Catalyst (ID)	$N_{\text{monolayer}}$ [ $\mu\text{mol} \cdot \text{g}^{-1}$ ]	Adsorption order n	$R^2$	$S_{\text{propane}}$ [ $\text{m}^2 \cdot \text{g}^{-1}$ ]	$S_{\text{N}_2}$ [ $\text{m}^2 \cdot \text{g}^{-1}$ ]
M1-a (5630)	34.9 (2)	1.15 (3)	0.99951	8.2 (1)	6.6
M1-b (6059)	48.5 (8)	1.07 (1)	0.99991	11.3 (1)	8.8
M1-c (5737)	62.3 (6)	1.03 (2)	0.99986	9.9 (1)	13.4
$\text{MoO}_3$ (6267)	6.8	1	0.99873	1.6	1.79
$\text{V}_2\text{O}_5$ (7304)	2.4	0.8	0.9991	0.57	-
$\text{Nb}_2\text{O}_5$ (7236)	21.69	1	0.99957	5.1	44.99
$\text{TeO}_2$ (7604)	11.52	0.74 (7)	0.99918	2.7	1.43

Per  $\text{m}^2$  & in the region of Langmuir ads. the number of propane adsorption sites increases significantly for M1 catalysts compared to its bare components.  
→ a new quality of the solid has been achieved via compositional and structural complexity of M1 catalyst

- adsorption order of  $n > 1$  confirms an activated adsorption process
- slightly  $n \uparrow$  with increasing the selectivity  
→ transformation of propane mostly pronounced for the most selective M1-a
- $n = 1$  is indicative of non-dissociative adsorption  
→ pure oxide components are inactive over propane
- $S_{\text{propane}} \sim S_{\text{N}_2}$

In contrast to  $\text{N}_2$  adsorption at 77 K, nearly the same monolayer adsorption capacities of 40-50  $\mu\text{mol/g}$  can be estimated for three M1 catalysts, and hence their surface areas are well comparable.

## Integral heat of desorbed propane

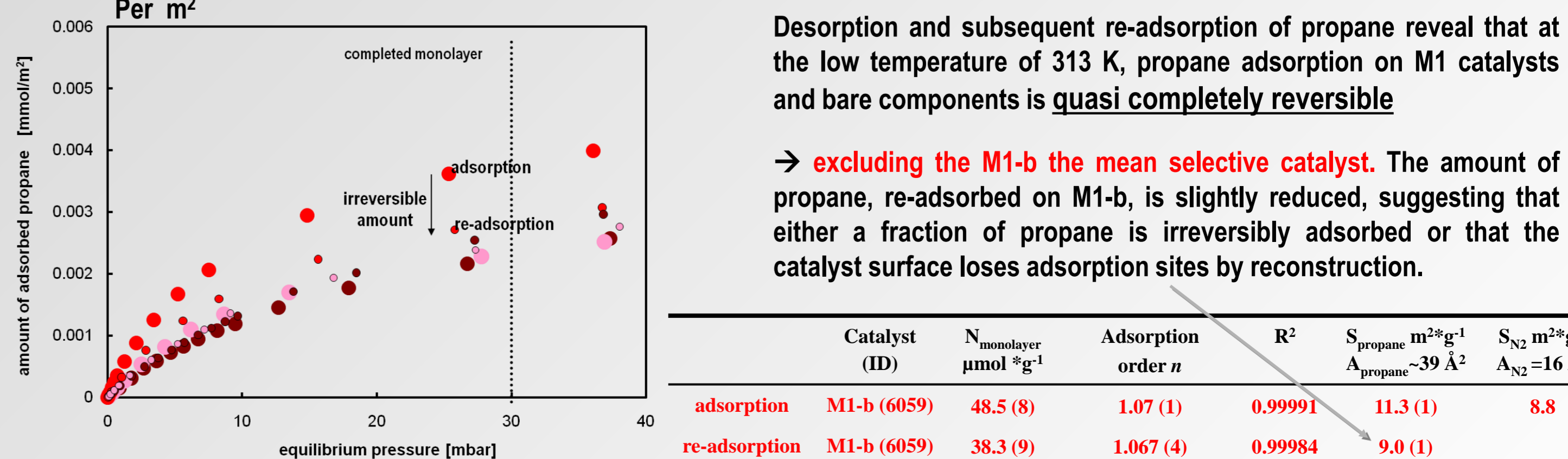


Adsorption  
 $\Sigma q_{\text{int}}(\text{Ads.}) = 7892 \text{ mJ}$  for 0.006 mmol/ $\text{m}^2$   
 $q_{\text{int}}(\text{Des.}) = -6560 \text{ mJ}$

Re-adsorption  
 $\Sigma q_{\text{int}}(\text{Ads.}) = 1557 \text{ mJ}$  for 0.004  $\mu\text{mol}/\text{m}^2$   
 $q_{\text{int}}(\text{Des.}) = -1534 \text{ mJ}$

For MoVTeNb oxide catalysts and its bare components the integral desorption heat is comparable to the sum of the heats for the individual adsorption steps  
→ propane is reversibly adsorbed at 313 K  
except for the mean selective M1-b catalyst  
→ propane is partial irreversibly adsorbed at 313 K

## Propane re-adsorption isotherm



Desorption and subsequent re-adsorption of propane reveal that at the low temperature of 313 K, propane adsorption on M1 catalysts and bare components is quasi completely reversible

→ excluding the M1-b the mean selective catalyst. The amount of propane, re-adsorbed on M1-b, is slightly reduced, suggesting that either a fraction of propane is irreversibly adsorbed or that the catalyst surface loses adsorption sites by reconstruction.

Catalyst (ID)	$N_{\text{monolayer}}$ [ $\mu\text{mol} \cdot \text{g}^{-1}$ ]	Adsorption order n	$R^2$	$S_{\text{propane}}$ [ $\text{m}^2 \cdot \text{g}^{-1}$ ]	$S_{\text{N}_2}$ [ $\text{m}^2 \cdot \text{g}^{-1}$ ]
adsorption M1-b (6059)	48.5 (8)	1.07 (1)	0.99991	11.3 (1)	8.8
re-adsorption M1-b (6059)	38.3 (9)	1.067 (4)	0.99984	9.0 (1)	-

## References

[1] M. Baca, A. Pigamo, J. L. Dubois, J. M. M. Millet, Topics in Catalysis 23 (2003) 39-46.  
[2] P. Beato, A. Blume, F. Girgsdies, R. E. Jentoft, R. Schlögl, O. Timpe, A. Trunschke, G. Weinberg, Q. Basher, F. A. Hamid, S. B. A. Hamid, E. Omar, L. Mohd Salim, Appl. Catal. A 307 (2006) 137-147.  
[3] A. Celaya Sanfiz, T.W. Hansen, A. Sakthivel, A. Trunschke, R. Schlögl, A. Knoester, H.H. Brongersma, M.H. Looi, S.B.A. Hamid, Journal of Catalysis, 258 (2008) 35-43.  
[4] L.C. Jozefowicz, H.G. Karge, E.N. Coker, J. Phys. Chem. 98 (1994) 8053-8060.  
[5] E.N. Coker, H.G. Karge, Rev. Sci. Instr. 68 (1997) 4521.  
[6] I. Langmuir, J. Am. Chem. Soc. 38 (1916) 2221.  
[7] A. L. McClellan, H. F. Harnsberger, J. of Colloid and Interface Science, 23 (1967) 577  
[8] A. Kamper, A. Auroux and M. Baerns, Physical Chemistry Chemical Physics, 2 (2000) 1069-1075.  
[9] A. Dinse, S. Khennache, B. Frank, Ch. Hess, R. Herbert, S. Wrabetz, R. Schlögl, R. Schomäcker, sub. 2008.  
[10] S. Wrabetz, James Mc Gregor, current project.  
[11] M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, Topics in Catalysis 23 (2003) 39.

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