

Supporting Information

Phase-pure M1 MoVNbTeO_x/TiO₂ nanocomposite catalysts: highly catalytic performance for oxidative dehydrogenation of ethane

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Experimental

Calculation of the kinetic parameters of reduction/re-oxidation. The performance of the pulse operation of the packed bed reactor is predicted by modeling a single tube, assuming that all tubes behave almost identically in a reliable manner^{S1,S2}. This work simulates the performance of the samples catalytic formulation during the pulse injection reaction in a single packed bed reactor in an isothermal mode. The one-dimensional axial model was used and given as Eqs. (S1-S5):

Gas phase:

Ethane pulse injection:

$$\frac{\partial p_{C_2H_6}}{\partial t} = -\frac{u}{\varepsilon_b} \frac{\partial p_{C_2H_6}}{\partial z} + D_z \frac{\partial^2 p_{C_2H_6}}{\partial z^2} - \frac{(1 - \varepsilon_b)}{\varepsilon_b} RT \rho_{cat} r_1 C_{ox} \quad (S1)$$

$$\frac{\partial p_{C_2H_4}}{\partial t} = -\frac{u}{\varepsilon_b} \frac{\partial p_{C_2H_4}}{\partial z} + D_z \frac{\partial^2 p_{C_2H_4}}{\partial z^2} + \frac{(1 - \varepsilon_b)}{\varepsilon_b} RT \rho_{cat} r_1 C_{ox} \quad (S2)$$

Oxygen pulse injection:

$$\frac{\partial p_{O_2}}{\partial t} = -\frac{u}{\varepsilon_b} \frac{\partial p_{O_2}}{\partial z} + D_z \frac{\partial^2 p_{O_2}}{\partial z^2} - \frac{(1 - \varepsilon_b)}{\varepsilon_b} RT \rho_{cat} r_o C_{red}$$

(S3)

Solid phase:

Ethane pulse injection:

$$\frac{\partial C_{red}}{\partial t} = r_1 (C_t - C_{red})$$

(S4)

Oxygen pulse injection:

$$\frac{\partial C_{ox}}{\partial t} = 2r_2 (C_t' - C_{ox})$$

(S5)

The postulated model expressions in Eqs. (S1-S5) are nonlinear. The numerical integration of the partial differential equations system was performed by using the MATLAB function ‘pedpe’. The optimization criteria were based on the fact that all the rate constants for each reaction must be positive and established on a minimum sum of squares of errors, given by Eq. (S6):

$$SSQ = \sqrt{\sum_{i=1}^N (\text{Conversion}_{i,\text{exp}} - \text{Conversion}_{i,\text{theo}})^2}$$

(S6)

The initial values of parameters were calculated by ethane conversion, inlet pressure, and lattice oxygen concentration of the first pulse. Because the conversion of ethane/oxygen was smaller than 2% after the 5th pulse, it may be related to the lattice oxygen diffusion process from the bulk phase to the surface. Then, the data of the first three pulses were used for fitting. The lattice oxygen capacity and oxygen vacancy capacity were estimated by the corresponding titration process. During ethane pulse

injection reaction, the catalyst structure may suffer from severe damage. So the lattice oxygen capacity may decrease after the ethane pulse reaction. Parameter discrimination was based on the lowest sum of square (SSQ) and the correlation coefficients (R^2) criteria.

Calculation of the active sites. The active site (V^{5+}) is calculated by Eq. (S6), which is determined by BET, XPS, and structure parameters from reference [S3]. The lattice parameter is listed in Table S1.

$$\begin{aligned} \text{Number of Active sites } (V^{5+}) &= \frac{1 \times \text{Specific surface area} \times \text{Bottom surface area} \times N_{001} \times MF_{M1}}{(1 + V^{5+}/V^{4+}) \times \text{Bottom surface area} + \text{Lateral surface area} \times A_{001}} \end{aligned} \quad (S7)$$

N_{001} is the number of V atom in each ab plane, A_{001} is the area of 001 plane in the cell, and MF_{M1} is the mass fraction of M1 phase in the catalyst.

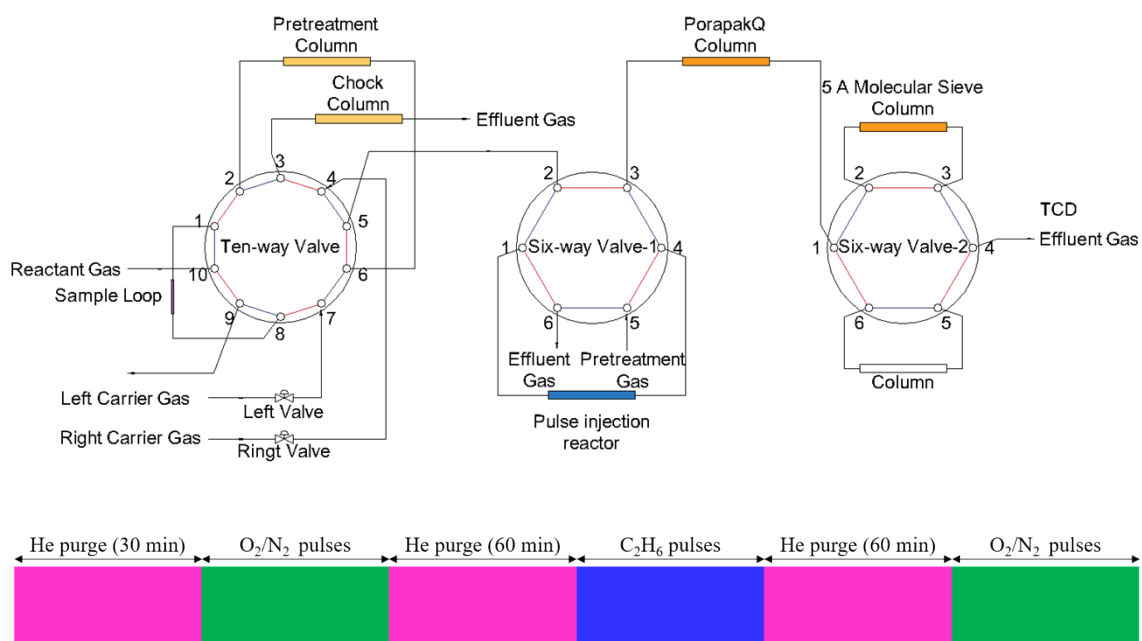


Fig. S1 The diagram for pulse reaction experiments

Note: Pulses of reactant gas was introduced by a 150 μ L (6.13 μ mol) sample loop, connected with a ten-way valve. The pulse injection reactor was introduced into the on-

line GC system by the six-way valve-1.

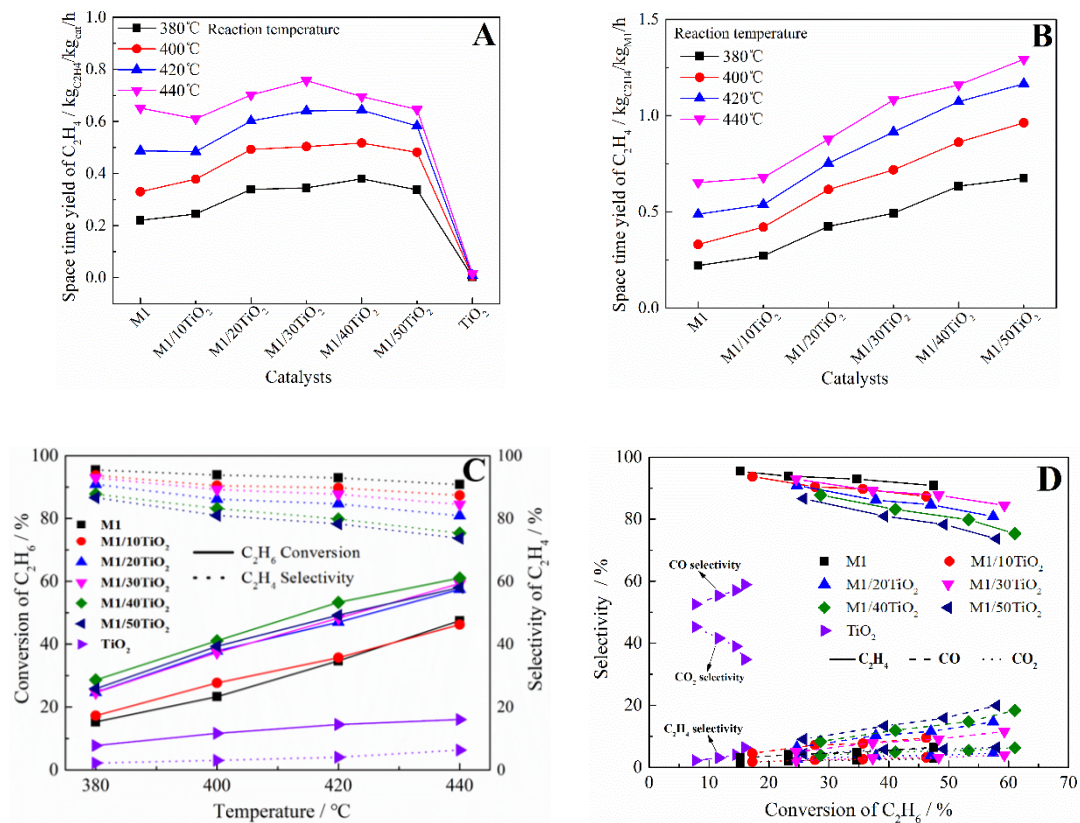


Fig. S2 Catalytic performance of a series of M1/TiO₂ catalysts with different reaction temperature
 (A) STY of M1/TiO₂ catalysts with different TiO₂ mass fractions.
 (B) STY of M1/TiO₂ catalysts with different TiO₂ mass fractions normalized to M1.
 (C) The conversion of C₂H₆ as a function of the reaction temperature T.
 (D) The selectivity of C₂H₄ as a function of the conversion of C₂H₆.

Reaction condition: atmospheric pressure, contact time W/F=18.52 g_{cat}·h/mol_{C₂H₆}, reaction temperature T=380-440 °C, reactants molar ratio C₂H₆/O₂/He=30/20/50

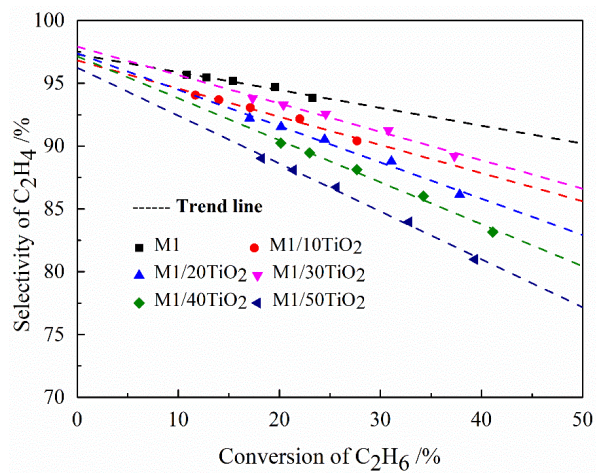


Fig. S3 Ethane conversion vs. selectivity and trend line of M1, M1/10~50TiO₂ at a reaction temperature of 400 °C , C₂H₆/O₂/He molar ratio of 30/20/50 at the reactor inlet, ambient pressure

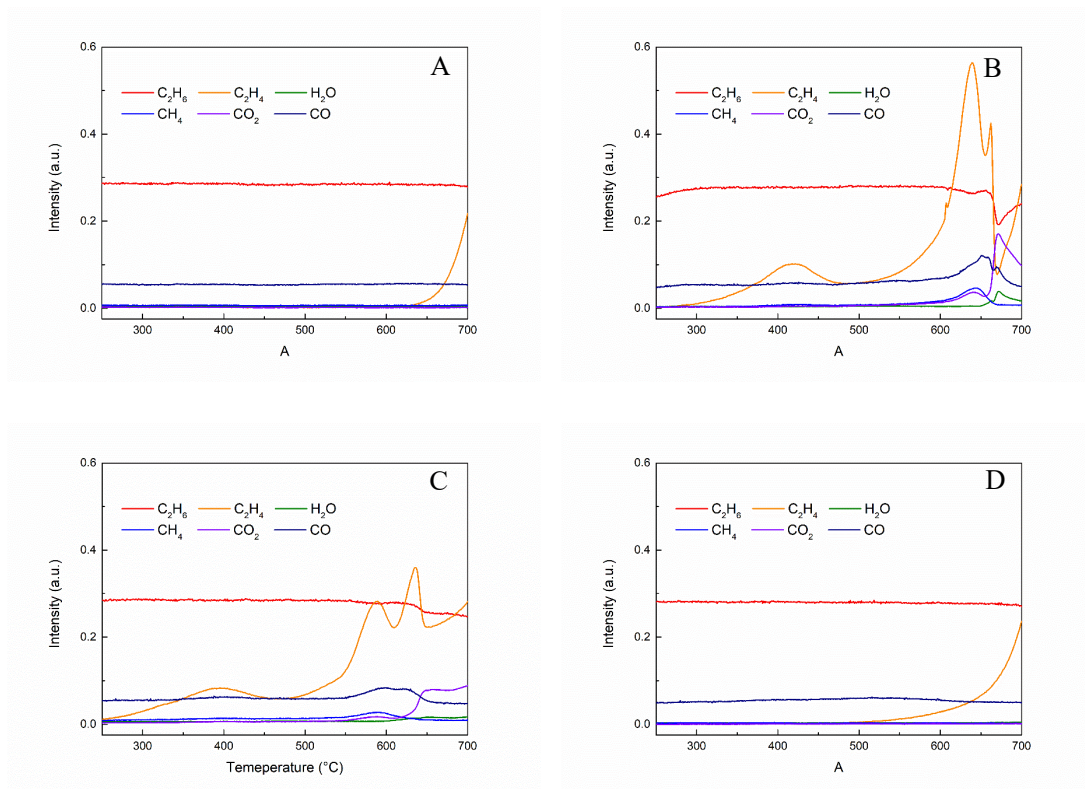


Fig. S4 C_2H_6 -TPSR profiles of (A) Empty, (B) M1, (C) M1/40TiO₂, and (D) TiO₂ catalyst

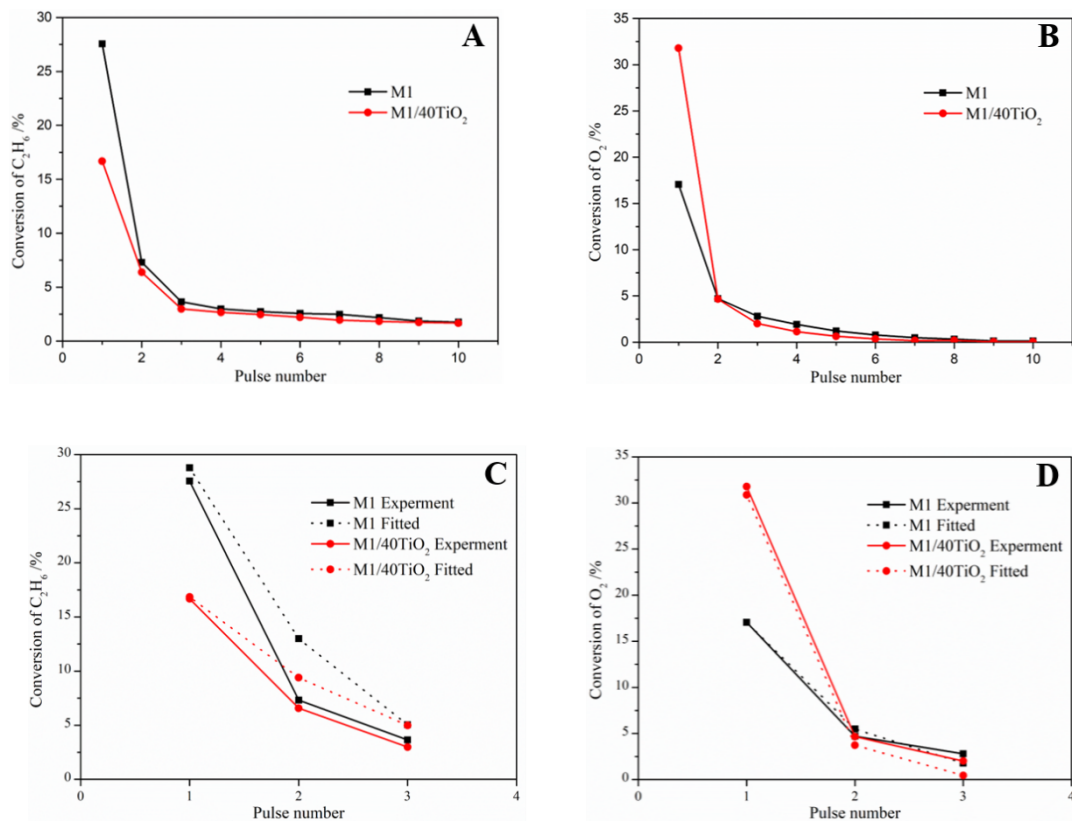


Fig. S5 Conversion of ethane (A) and oxygen (B) pulse injection reaction, ethane (C) and oxygen (D) pulse injection reaction fitted results. (reaction condition: reaction temperature of 400 °C, rate of carrier gas 30 ml/min, mass of catalyst 20 mg, pulse gas 6.13 μ mol per time, pure C_2H_6 or 50%/50% O_2/N_2 , reaction pressure of 525 kPa)

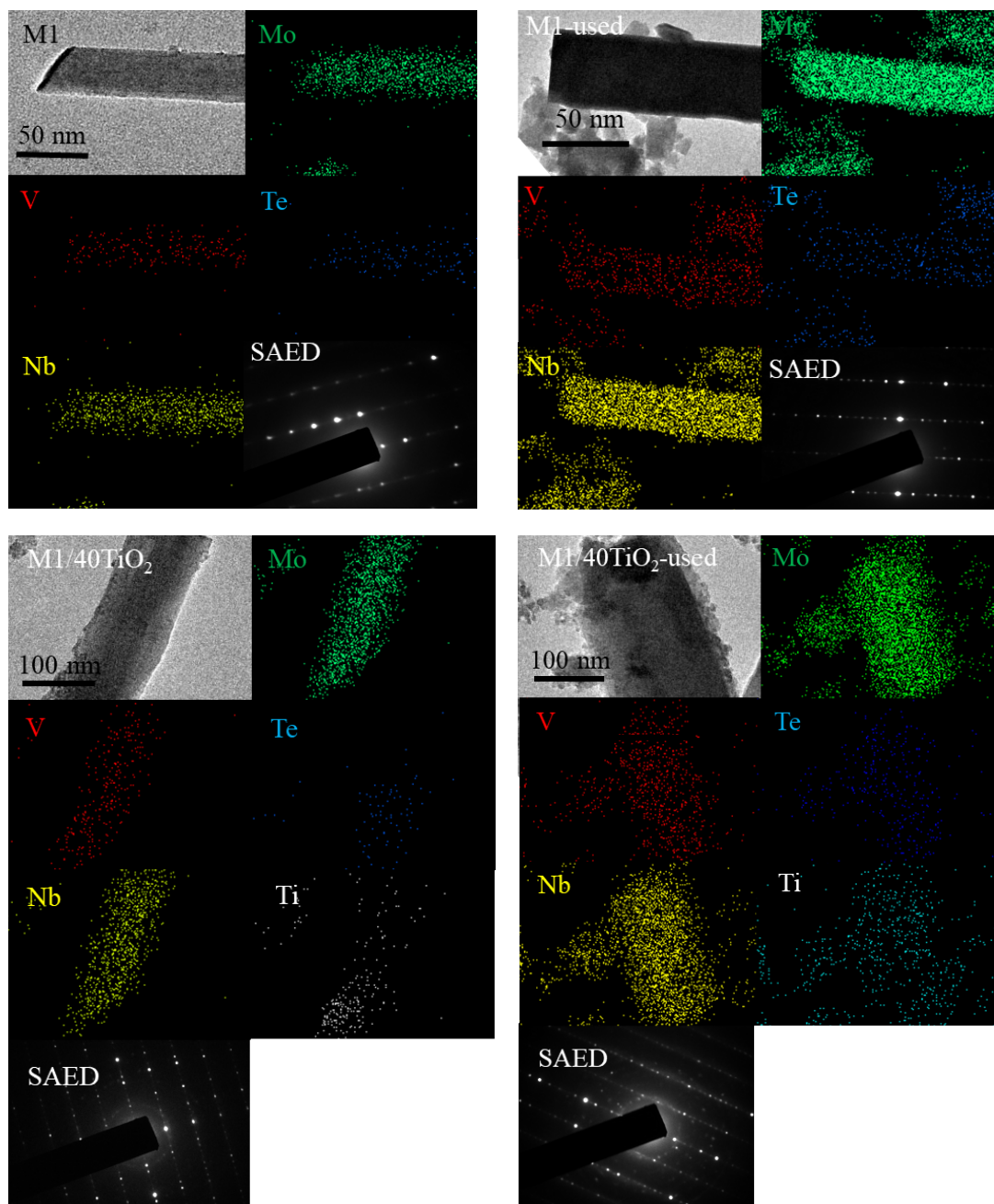


Fig. S6 Elemental mapping images of Mo, V, Te, Nb, and Ti and corresponding selected area electron diffraction (SAED) patterns.

Table S1 Catalytic performance of M1, M1*, and M1/40TiO₂ for ODHE reaction ^a

Catalyst		C ₂ H ₆ conversion (%)	Products distribution (%)		
			C ₂ H ₄	CO	CO ₂
1	M1	23.3	94.8	3.4	1.8
2	M1*	27.4	94.4	3.6	2.0
3	M1/40TiO ₂	41.4	83.2	11.9	4.9

^a Reaction condition: reaction temperature T = 400 °C, contact time W/F= 18.52 g_{cat}·h/mol_{C₂H₆}, ambient pressure, C₂H₆/O₂/He (inlet) = 30/20/50 (6/4/10 NmL/min)

Table S2 Parameter of M1 MoVNbTeO_x ^{S3}

Catalysts	Lattice parameter (Å)			Particle Size (nm)		N_{001}
	a	b	c	Width	Length	
MoVNbTeO _x	21.1337	26.6440	4.01415	~80	~200	6

Table S3 Trend line intercepts and slopes of catalysts

Catalysts	Intercept %	Slope
M1	97.31	-0.142
M1/10TiO ₂	96.82	-0.224
M1/20TiO ₂	97.38	-0.289
M1/30TiO ₂	97.92	-0.226
M1/40TiO ₂	97.15	-0.334
M1/50TiO ₂	96.24	-0.381

Table S4 Lattice parameters of phase-pure M1 MoVNbTeO_x/TiO₂ catalysts

Catalyst	M1 lattice parameters ^a (Å)			TiO ₂ d ₁₀₁ (Å) ^b	TiO ₂ ^c
	a	b	c		Particle size (nm)
M1	21.1801	26.6342	4.0072	-	-
used M1	21.0239	26.4554	4.0019	-	-
M1/20TiO ₂	21.2172	26.6369	4.0124	3.5328	13.68
used M1/20TiO ₂	21.2807	26.8275	4.0225	3.5409	14.52
M1/40TiO ₂	21.1320	26.7751	4.0107	3.5429	11.75
used M1/40 TiO ₂	21.1143	26.7834	4.0107	3.5283	14.78
M1/50TiO ₂	21.2553	26.5977	4.0060	3.5225	11.87
used M1/50TiO ₂	21.1901	26.6793	4.0123	3.5260	14.48
TiO ₂	-	-	-	3.5613	14.49
used TiO ₂	-	-	-	3.5162	16.56

^a Determined by fitting XRD patterns based on the M1 phase (ICSD 55097).

^b Determined by fitting XRD patterns based on the anatase TiO₂ (JPDS 21-1272).

^c Determined based on the half band width of peak at 25.4° in XRD patterns to calculate the average crystal size along the [1 0 1] crystal direction by Scherrer equation.

Table S5 Textural characterization of the phase-pure M1 MoVNbTeO_x/TiO₂ catalysts

Catalysts	Specific surface area m ² /g	Pore Volume cc/g
M1	17.7	0.060
Used M1	15.7	0.048
M1/20TiO ₂	33.4	0.072
Used M1/20TiO ₂	31.0	0.069
M1/40TiO ₂	52.4	0.085
Used M1/40TiO ₂	50.0	0.080
TiO ₂	52.7	0.104
Used TiO ₂	43.8	0.099

Notes and references

- S1. A. I. Anastasov, Chemical Engineering Science, 2003, **58**, 89-98.
- S2. G. F. Froment, Chemie Ingenieur Technik - CIT, 1974, **46**, 374-386.
- S3. P. DeSanto, D. J. Buttrey, R. K. Grasselli, C. G. Lugmair, A. F. Volpe, B. H. Toby and T. Vogt, Z. Kristall., 2004, **219**, 152-165.