

Supplementary Information

1. Preparation methods for iron-alumina catalysts

Type A catalysts were prepared by the impregnation of böhmite (high-purity dispersible böhmite, Dispersal by Sasol) with a solution of ammonium iron(III) citrate; 5 g of böhmite powder was impregnated with 3.5 ml of the aqueous solution of 1.8 and 3.7 g of ammonium iron(III) citrate (p.a., 14.5–16% Fe, Fluka). The as-prepared samples were left to dry at 120 °C for 4 h followed by calcination at 950 °C for 4 h producing Fe/Al₂O₃ catalysts containing 5 and 10 wt.% of Fe, denoted throughout the manuscript as 5Fe/Al₂O₃-A and 10Fe/Al₂O₃-A, respectively.

Type B catalysts were prepared by impregnating 5 g of alumina powder, obtained by calcination the above-described böhmite at 1100 °C for 10 h, with 3.5 ml of a solution containing 0.3, 1.8, and 3.7 g of ammonium iron(III) citrate in distilled water. The prepared materials had approximately 1, 4, and 9 wt.% of Fe and are abbreviated as samples 1Fe/Al₂O₃-B, 4Fe/Al₂O₃-B and 9Fe/Al₂O₃-B, respectively. These samples were dried at 120 °C and calcined 950 °C for 4 hours in both steps.

Type C catalyst was prepared by impregnating the freshly prepared amorphous AlO(OH) suspension and by using an acidic FeCl₂ solution as the iron source. Hydrated amorphous aluminium oxide was precipitated from solution of ammonium aluminium sulphate by ammonia; the formed solid was filtered and mixed with distilled water, 25% aqueous solution of ammonia (up to pH=10.7), böhmite seeds (mass ratio H₂O:NH₃: böhmite seeds = 1:1:0.02). After 6 days aging AlO(OH) with böhmite crystallinity was received. After filtration and washing with distilled water fresh prepared AlO(OH) was impregnated using the solution containing: FeCl₃, 35% HCl, and distilled water with the mass ratio 1:1.5:10, respectively. The suspension was dried in spray dryer. The final step of the preparation of 4Fe/Al₂O₃-C catalyst was calcination at 950 °C for 4 h.

Table S1. Surface area of selected iron-alumina catalysts.

Type of catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
5Fe/Al ₂ O ₃ -A	65.3
10Fe/Al ₂ O ₃ -A/12	70.3
4Fe/Al ₂ O ₃ -B	33.7
4Fe/Al ₂ O ₃ -B/12	28.0

2. Material characterization

Figures S1 shows the XRD patterns of the catalysts prepared by different methods in described Section 1 for samples containing 10% of Fe. The diffraction patterns show intensive and sharp diffraction peaks at $2\theta = 16.3, 19.6, 31.3, 32.8, 36.7, 39.9, 44.8, 47.7, 50.7, 59.9$, and 67.5° , which are characteristic of monoclinic θ -Al₂O₃ phase, and at $2\theta = 25.6, 35.1, 37.7, 43.4, 57.5$ and 66.5° corresponding to the crystal structure of α -Al₂O₃ phase labelled with θ and α , respectively. The lines of δ -Al₂O₃ are in prevailing cases covered to each other with θ - and α -Al₂O₃ lines and can be separately observed only at $2\theta = 45.4^\circ$. The characteristic diffraction peaks of Fe₂O₃, marked by the crosses in Figure S1, are observed at $2\theta = 24.3, 33, 35.5, 39.5, 41, 43.5, 49.5, 54.1, 57.5, 62.3, 64$ and 69.5° .

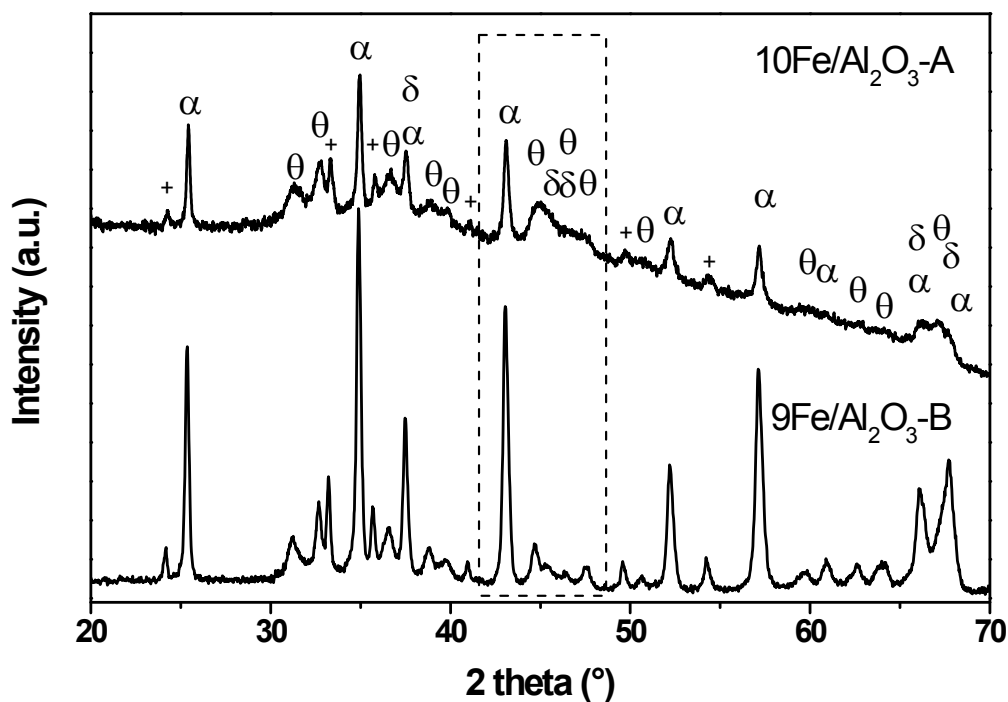


Figure S1. XRD patterns showing the influence of the preparation method on the final type of alumina modifications for $\sim 10\%$ of Fe (the Greek symbols correspond to alumina modifications and cross to Fe_2O_3).

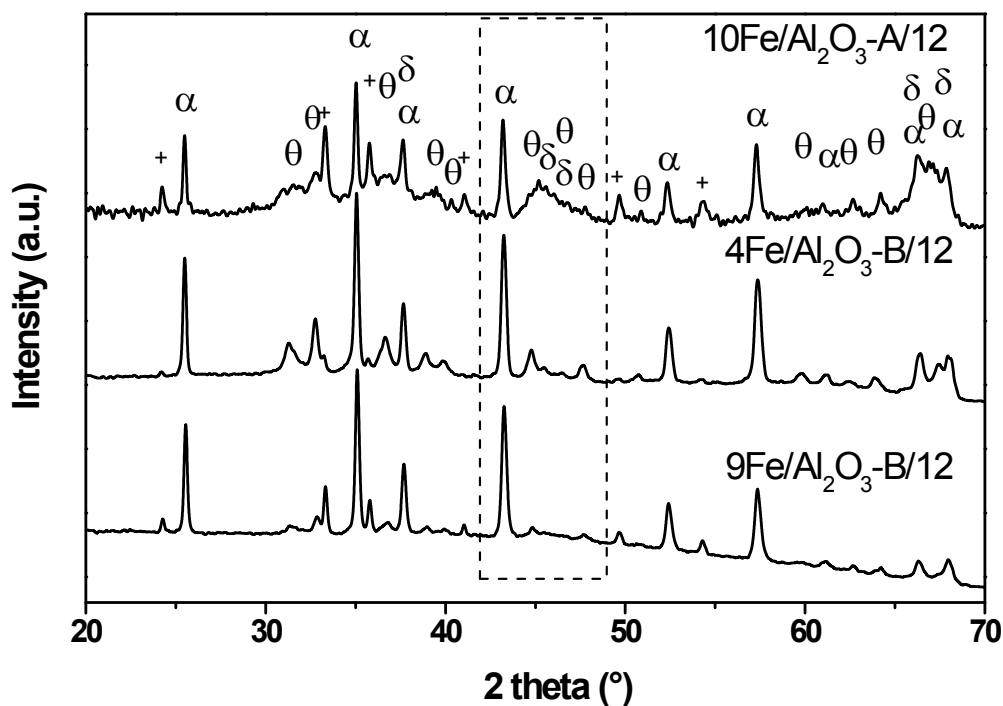


Figure S2. XRD showing Fe/Al₂O₃ catalyst after 12 days aging (the Greek symbols correspond to alumina modifications and cross to Fe₂O₃).

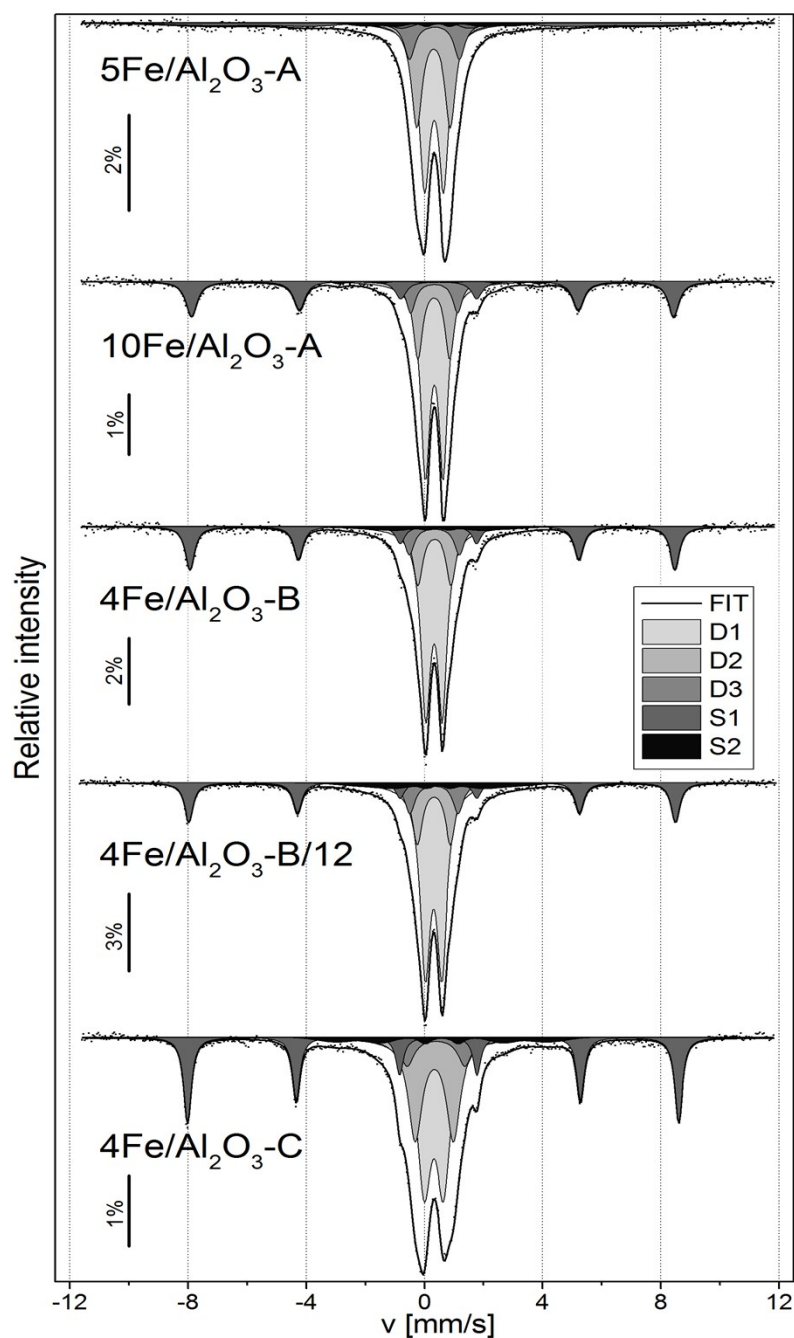


Figure S3. Mössbauer spectra of Fe species in Fe/Al₂O₃ catalysts measured at room temperature.

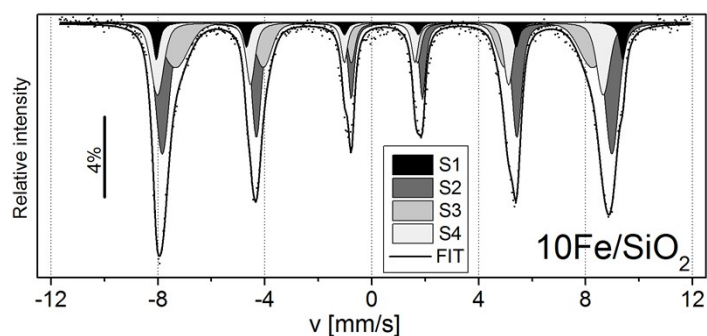


Figure S4. Mössbauer spectra of Fe species in Fe/SiO₂ catalyst measured at 4.2 K.

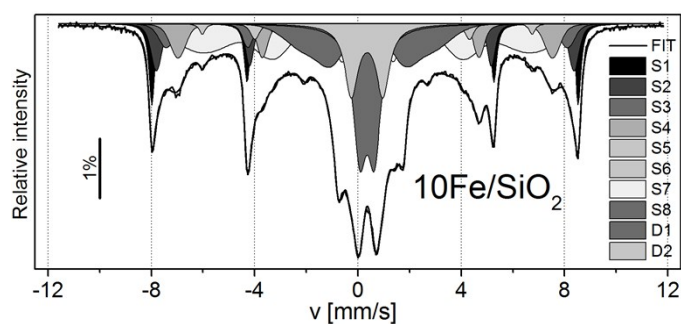


Figure S5. Mössbauer spectra of Fe species in Fe/SiO₂ catalyst measured at RT.

Table S2

Mössbauer parameters and spectral contributions of Fe species in Fe/SiO₂ catalyst recorded at 4.2 K

Sample		IS	QS	B_{hf}	Rel.	Fe species
		(mm s ⁻¹)	(mm s ⁻¹)	(T)	(%)	
Fe/SiO ₂	S1	0.51	0.31	54.2	9	Hematite Fe ₂ O ₃ > 10nm
	S2	0.29	0.03	51.9	21	Hematite-like Fe _{2-x} Si _x O ₃
	S3	0.56	0.01	52.2	44	Maghemite-like Fe _{2-x} Si _x O ₃
	S4	0.46	-0.03	48.4	26	Hematite-like Fe _{2-x} Si _x O ₃

3. Catalytic tests

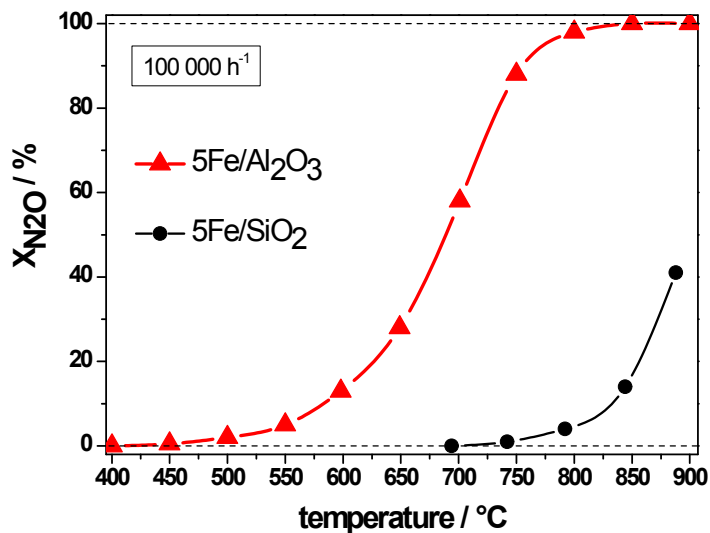


Figure S6. HT-N₂O decomposition over 5Fe/SiO₂ compared with 5Fe/Al₂O₃.

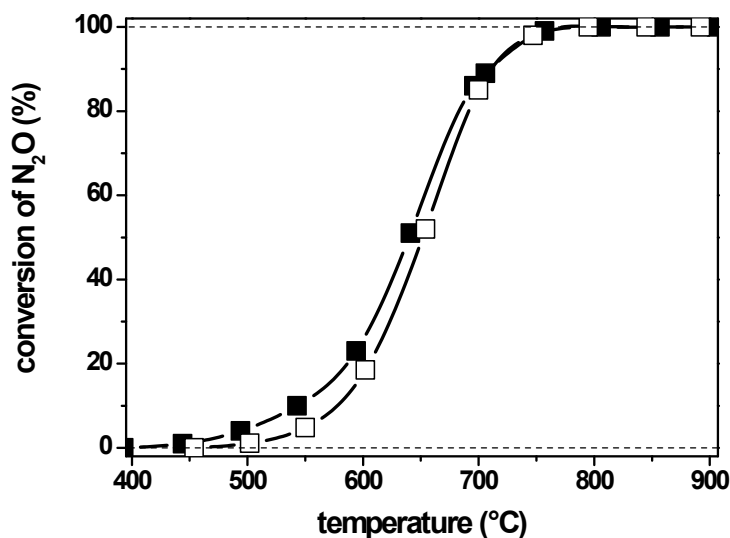


Figure S7. Influence of NO gas on the catalytic activity of 4Fe/Al₂O₃-B catalyst: feed with NO (full squares) and without NO (empty squares).

4. Reaction rate, normalized T_{X50} and rate over Fe active species

The reaction rate could not be calculated directly from a simple assumption of a differential reactor because of the high N₂O conversions of over 20% at temperature used for

catalysts activity comparison ($T_{\text{ref}}=650\text{ }^{\circ}\text{C}$). Instead, the initial reaction rate was used to calculate the reaction rate according to:

$$r_{N_2O}^0 = k_{\text{ref}} p_{N_2O}^0,$$

where k_{ref} is the estimated rate constant from experimental data (assuming an integral reactor) and $p_{N_2O}^0$ is the initial N_2O partial pressure.

Experiments in this study were carried out at constant VHSV (100 000 h^{-1}) which means that the catalyst mass in catalytic experiments varied as the catalyst density was different for studied Fe-alumina samples. In order to make the T_{X50} parameter more suitable for catalyst performance ranking we proceeded to the normalization of the T_{X50} to constant catalyst mass. The normalized T_{X50} was evaluated from parameters (E_A and k_{ref}) estimated from experimental data by solving the following nonlinear equation:

$$f(T) = 0 = \int_0^{X=50} \frac{dX_{N_2O}}{p_{N_2O}(X)} + \frac{m_{\text{cat}} k}{F_{N_2O}^0},$$

where the $k = k_{\text{ref}} \exp \{ -E_A / (R(T_{\text{ref}} + 273.15))((T_{\text{ref}} + 273.15)/(T_{X50} + 273.15) - 1) \}$, $F_{N_2O}^0$ is the N_2O inlet molar flow and the catalyst mass m_{cat} was arbitrarily set to 0.1 g in order to compare experiments carried out with different catalyst masses but the same GHSV.

5. Internal mass transport effects

Internal diffusion effect was estimated for the samples with high catalytic activity (5Fe/ Al_2O_3 -A, 10Fe/ Al_2O_3 -A and 4Fe/ Al_2O_3 -B). These catalysts are expected to suffer from relatively important intraparticle diffusion resistance at higher temperatures. The structural parameters necessary for the calculation were obtained by Hg intrusion porosimetry and they are listed in table S3.

Table S3. Structural parameters of the catalyst and catalyst particle obtained from Hg intrusion porosimetry.

Sample	Catalyst and catalyst particle properties (Hg porosimetry)
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	r_p/mm	$\epsilon_p/-$	$\rho_{\text{cat}}/\text{g cm}^{-3}$	d_p/nm
5Fe/Al ₂ O ₃ -A	0.2	0.494	2.80	23.2
10Fe/Al ₂ O ₃ -A	0.2	0.682	2.91	48.6
4Fe/Al ₂ O ₃ -B	0.2	0.449	2.93	42.0

The effect of internal diffusion on the apparent reaction rate could be expressed as

$$r_{N_2O} = \eta k_I p_{N_2O}, \quad (1)$$

where k_I is the intrinsic rate constant and η is the effectiveness factor which is the function of the Thiele modulus (θ_T) and the Biot number (B) [1]

$$\eta = \frac{1}{\theta} \left[\frac{1/\tanh(3\theta_T) - 1/(3\theta_T)}{1 + \theta_T(1/\tanh(3\theta_T) - 1/(3\theta_T))/B} \right]. \quad (2)$$

The Biot number (dimensionless mass-transfer coefficient) is given as

$$B = k_g r_p / D_{N_2O,He}, \quad (3)$$

where k_g is the external-mass transfer coefficient evaluated from usual dimensionless criteria [2] and diffusion coefficient $D_{N_2O,He}$ was obtained according to the Fuller's method [3]. The Thiele modulus is written as

$$\theta = \frac{d_p}{2} \sqrt{\frac{(1 - \epsilon_p) \rho_{\text{cat}} RT k_I}{D_{\text{eff}}}}, \quad (4)$$

where D_{eff} is the effective diffusivity, ϵ_c and ρ_c are the catalyst porosity and density, respectively. The amount of He is ~95% and the effective diffusivity can be calculated as the contribution of the diffusion coefficient of N₂O in He, $D_{N_2O,He}$, and the Knudsen diffusion coefficient, D_K

$$D_{\text{eff}} = \left(\frac{1}{D_{N_2O,He}} + \frac{1}{D_K} \right)^{-1}. \quad (5)$$

where the Knudsen diffusion coefficient was obtained from

$$D_K = d_p \frac{\epsilon_p}{3\tau} \sqrt{\frac{8RT}{\pi M_{N_2O}}} \quad (6)$$

Intrinsic kinetic parameters were evaluated by a nonlinear regression using numerical integration of the mass balance of the PFR (plug flow reactor)

$$\frac{dF_{N_2O}}{dw} = -m_{CAT} \eta(T, X_{N_2O}) k_{I,ref} \exp \left\{ -E_I / (R(T_{ref} + 273.15)) ((T_{ref} + 273.15)/T - 1) \right\} p_{N_2O} \cdot \quad (7)$$

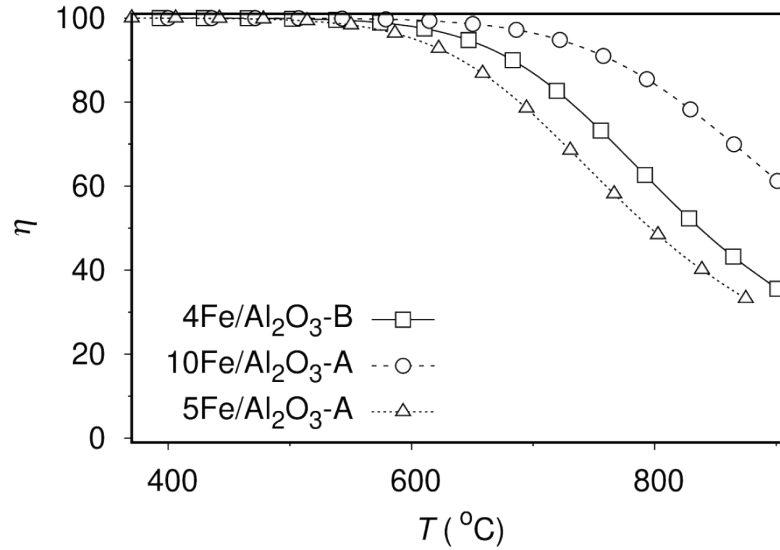


Figure S8. Effectiveness factor as the function of temperature for selected catalyst samples.

The influence of the internal diffusion on the calculated intrinsic parameters: activation energy, (E_I), and the rate constant, k_I , was the highest for the 5Fe/Al₂O₃-A and 4Fe/Al₂O₃-B samples. This is due to the low value of the effectiveness factor (approximately 40%) at high temperatures. Even for such a low effectiveness factor (figure S8), the differences between the apparent and intrinsic parameters were around 10% (see table S4). We, therefore, assumed the effect of the internal diffusion on the overall reaction rate as negligible.

Table S4. Effect of internal mass transport on calculated parameters; parameters estimated without the mass transport effects (k_{ref} , E_A) and with the mass transport effect ($k_{I,ref}$, E_I)

Sample	E_A	E_I	k_{ref}	$k_{I,ref}$
	kJ mol ⁻¹		nmol Pa ⁻¹ s ⁻¹ g ⁻¹	
5Fe/Al ₂ O ₃ -A	119	125	16.9	19.4
10Fe/Al ₂ O ₃ -A	152	155	14.6	14.9
4Fe/Al ₂ O ₃ -B	133	142	9.9	10.7

Table S5. Concentration of Fe in T_d and O_h coordination from Mössbauer spectra deconvolution and calculated rate of N₂O decomposition at 650 °C over Fe/Al₂O₃ analyzed by Mössbauer spectroscopy.

catalyst	Fe	r _{N2O}
	mmol g ⁻¹	m ² g ⁻¹
5Fe/Al ₂ O ₃ -A	0.245	1.71
4Fe/Al ₂ O ₃ -B	0.114	1.00
4Fe/Al ₂ O ₃ -B/12	0.093	0.69
4Fe/Al ₂ O ₃ -C	0.039	0.22

List of symbols

Symbol	Meaning	Unit
B	Biot number	-
d_p	mean pore diameter	m
D_{ij}, D_{eff}, D_K	binary, effective and Knudsen diffusion coefficient	m^2s^{-1}
E_A	activation energy	J mol^{-1}
E_I	intrinsic activation energy	J mol^{-1}
F	molar flow	mol s^{-1}
k	rate constant	$\text{nmol Pa}^{-1}\text{g}^{-1}\text{s}^{-1}$
k_I	intrinsic rate constant	$\text{nmol Pa}^{-1}\text{g}^{-1}\text{s}^{-1}$
k_g	external mass transfer coefficient	m s^{-1}
m	mass	g
M	molecular mass	$\text{mol kg}^{-1}, \text{mol g}^{-1}$
p	pressure	Pa
r	reaction rate	$\text{mol g}^{-1}\text{s}^{-1}$
r_p	catalyst particle radius	m
R	universal gas constant	$\text{J mol}^{-1}\text{K}^{-1}$
T	temperature	K
T_{X50}	temperature of 50% conversion	$^{\circ}\text{C}$
w	mass fraction or dimensionless mass	-
X	conversion	-
ε_p	catalyst particle porosity	-
η	effectiveness factor	-
π	Ludolph's number	-
ρ	density	kg m^{-3}
θ_T	Thiele modulus	-
τ	tortuosity	-
general subscripts		
cat	catalyst related value	
i	i -th component or	
N_2O	value related to N_2O	
ref	value at reference temperature (650°C)	
general superscripts		
0	value related to the inlet or beginning	

References

- [1] Rawlings, J., B., Chemical reactor Analysis and Design Fundamentals, 2002 ed., Nob Hill Publishing, LLC Madison, Wisconsin, 2002.
- [2] Bird, R., B., Stewart, W., E. and Lightfoot, E., N., Transport Phenomena, 2nd edition, Wiley&Sons, N.Y., 2002.

- [3] Lijten, C., C., M. , Bosschaart, K., J., VanDongen, M., E., H., Int. J. Heat Mass Transf. 40 (1997) 3497–3502.