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A structured test reactor for the evaporation of methanol on the basis of a catalytic combustion

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Abstract

The kinetics of the catalytic deep oxidation of methanol was studied in stacked segments of a turbulence insert (SSTIs) coated with Pt/γ-Al_2O_3 and Pt/zeolite catalysts. These geometries, which are termed a structured test reactor in the heading, are intended to replace plane expanded metal discs (PEMDs) used in the so-called catalytic burner at Research Centre Jülich, up to the present. The catalytic burner performs the low-pollution combustion inter alia of the anode exhaust gases of the fuel cell. SSTIs coated with Pt/γ-Al_2O_3 showed different kinetics for differential conversions as a function of temperature. At low reaction temperatures (100–130°C) ignition kinetics with a very high activation energy of 60.3 kJ/mol was found. In the further course of the reaction, the kinetically controlled reaction with an activation energy of 48.5 kJ/mol was observed. In the range of non-differential conversions, the activation energy decreased significantly, which suggests a limitation of the reaction process by mass transport phenomena. Compared to the PEMDs, clearly higher reaction rates were observed, which enable a reduction of the catalyst mass. This as well as the spatial structure of the SSTIs make it possible to achieve a reduction in volume and weight and thus improved dynamics in constructing a novel catalytic burner. The SSTIs coated with Pt/zeolite showed perceptibly lower reaction rates than the Pt/γ-Al_2O_3 substrates and could thus not compete with the PEMDs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methanol; Catalytic deep oxidation; Noble metals; Structured reactor; Ignition; Kinetics; Diffusion limitation

1. Introduction

If it is assumed that mobility should also constitute an important part of an individual's personal freedom in the coming decades, alternatives to the existing conventional concept of a passenger car engine with internal combustion of gasoline and diesel must be given consideration for several reasons.

From the economic perspective, it must be noted that the price of crude oil, which is processed into gasoline and diesel in refineries, will become increasingly higher in future, since petroleum resources are becoming scarcer and their development more and more expensive. In 1999, worldwide estimated petroleum reserves amounted to approximately 138 billion t with a total consumption of approximately 3.4 billion t in 1999 [1]. In addition, there is a strong demand for crude oil as the base product for numerous important chemical syntheses above all in the chemical industry inter alia in the field of polymers, fibres or solvents. In the long run, this will make it mandatory to greatly reduce the application of crude oil as the base product for gasoline and diesel in favour of its use, e.g., in synthetic chemistry. From the ecological point of view, private transport, which has drastically increased in the past few decades, has led to the emission of large amounts of environmentally

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harmful substances such as NO_x, CO, hydrocarbons and particulates. Since, the intensity of private transport is more likely to increase than decrease in the coming years, the legislation has drastically lowered the emission limits and will continue to do so in the future. Fuel cell technology for mobile applications has a large potential for meeting these economic and ecological challenges [2]. In order to be marketable, the volume, weight, dynamics, cost and range of an electric drive with fuel cell must be able to compete with conventional technology. If the current development status is compared, however, the specific weight of a state-of-the-art *compact reformer* (composed of methanol reformer and catalytic burner permitting the endothermic reforming reaction through the generation of low-pollution heat), e.g., amounts to approximately 4–7 $\mathrm{kg/kW_{mech.}}$. In order to be competitive, the specific weight of the compact reformer must not exceed 0.3 $\mathrm{kg/kW_{mech.}}$. This comprizes 0.17 $\mathrm{kg/kW_{mech.}}$ for the reformer and 0.13 $\mathrm{kg/kW_{mech.}}$ for the catalytic burner. This goal is to be achieved by a decisive improvement of the heat transfer inside the compact reformer. The innovative approach is the development of stacked segments of a turbulence insert (SSTIs) coated with catalyst, and this paper is concerned with the generation of heat, e.g., for the

Fig. 1. SSTI for the catalytic deep oxidation of methanol.

evaporation of methanol by means of the catalytic deep oxidation of methanol according to Eq. (1).

$$CH_3OH + 1.5\,O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

In the literature, a large number of different catalyst classes are described as being suitable for the total oxidation of hydrocarbons and alcohols [3–25].

2. Experimental setup

Twenty segments each 3.2 mm in width and 5.8 mm in thickness were cut from a conventional, corrugated turbulence insert with the aid of a laser. These segments were stacked on top of each other in a spatially separated manner and their length was matched with the flow diameter of the reactor (Ø 80 mm) (cf. Fig. 1). The SSTIs in Fig. 1 have an outer surface of approximately 450 cm^2. In order to study the total oxidation of methanol, the SSTIs were coated with two different catalysts (Pt/γ-Al_2O_3, Pt/zeolite), which had proved to be very active for this reaction [26]. The materials were manufactured and the coating applied by Engelhard. Since, the catalysts are proprietary ones nothing is known about their characteristics such as pore volume or metal dispersion.

The SSTIs were investigated in an adiabatically operated plug flow reactor. The reaction zone consists of five SSTIs connected behind each other and coated with increasing amounts of the above-mentioned catalytically active materials in the direction of flow ($m_{\mathrm{Pt}} = 0.20$–0.28 mg, $m_{\mathrm{support}} = 2$ g). The geometrical dimensions of all stages are identical. Depending on the inlet temperature and concentration of the methanol fuel gas and on the catalyst mass, concentration and temperature profiles are established along the flow length of the reactor. The graduation of the catalyst coating aims at establishing a differential conversion of methanol at each reaction stage. In the case of loading with Pt/γ-Al_2O_3, the reaction temperatures were varied between 100 and 170°C and the methanol concentrations upon entering the first stage between 1345 and 2466 ppm. In the case of Pt/zeolite loading, the measurements covered the ranges between 150 and 250°C as well as between 1793 and 3586 ppm of methanol. The oxidation medium was air ($\lambda = 38.9$–104.0). The experiments were carried out at atmospheric pressure. The total volume flow was 250 l/min in all measurements. Between the stages there are tapping points at which partial flows of the product gas can be extracted for gas chromatographic analysis. Moreover, the reaction temperatures are measured at these points. With the aid of a Levenberg–Marquardt algorithm the apparent activation energy E_{A}, the preexponential factor k_0 and the reaction order n for methanol were determined according to the following formal kinetics formulation:

$$r = k_0 \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right) c_{\mathrm{MeOH}}^{n}$$

3. Results and discussion

3.1. *Pt/γ-Al_2O_3-coated SSTIs*

Fig. 2 illustrates that two different reaction processes take place in the range of differential conversions. The catalytic ignition of the methanol–air mixture has its own kinetics with a high activation energy of 60.3 kJ/mol. Oxygen and methanol compete for the adsorption sites and the reaction order with respect to methanol amounts to 0.5. After the reaction has been ignited, the kinetically controlled reaction ($X < 12\%$) starts on the catalyst surface. It proceeds according to a different mechanism at higher rate constants in the entire temperature range examined and has a lower activation energy of 48.5 kJ/mol than the ignition. The reaction order for methanol in this case is 1.4. Non-differential conversions greater than 12% lead to a drastic decrease of the activation energy to 18.1 kJ/mol and to a further increase of the rate constant in the entire temperature range, whereas the reaction order for methanol does not change. Due to the higher rate constant, the chemical reaction becomes much faster than the diffusion of the educts into the pore system of the catalyst. As a consequence, the apparent activation energy is less than half the value found without inhibition due to pore diffusion. Fig. 2 as well contains 95% confidence intervals for the fitted data as found from Levenberg–Marquardt algorithms for the diffusion limited reaction and the kinetics of the ignition on Pt/γ-Al_2O_3. They are exemplary for all presented graphs.

In the literature, activation energies of 59–64 [14], 56 [13] and 48 kJ/mol [16] are measured for

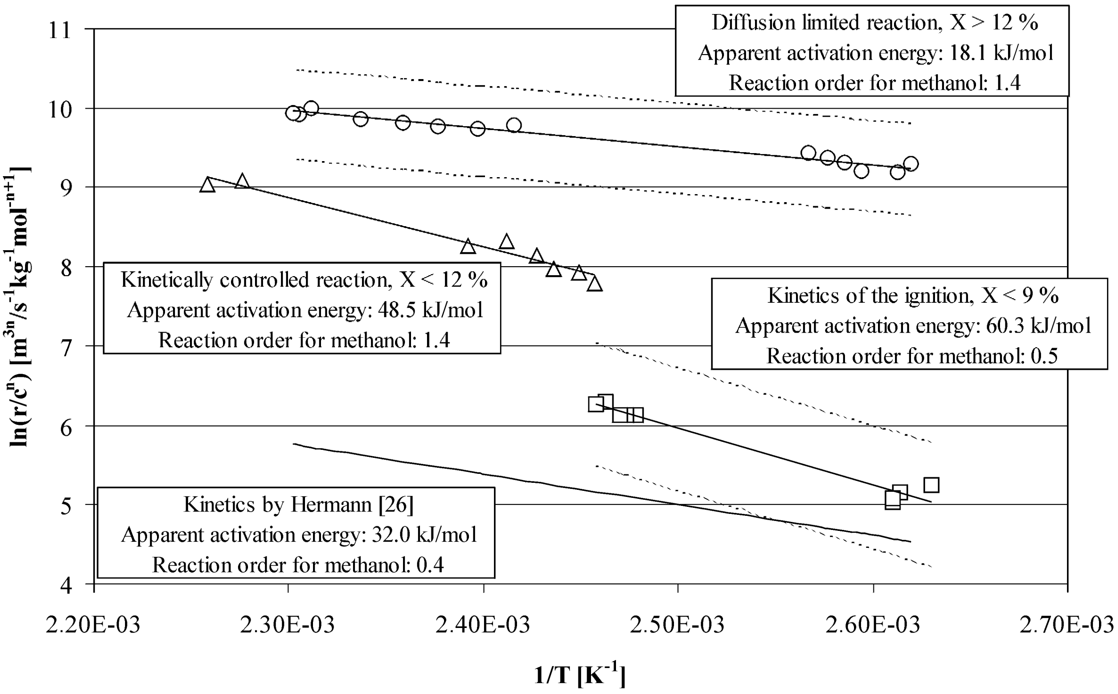

Fig. 2. Arrhenius plot for catalytic deep oxidation of methanol in Pt/γ-Al_2O_3 containing SSTI compared with literature, $T = 373$–443 K, $c_{0\,\mathrm{MeOH}} = 1345$–2466 ppm, $m_{\mathrm{Pt}} = 0.20$–0.28 mg, $m_{\mathrm{Al_2O_3}} = 2$ g.

the methanol total oxidation on Pt catalysts without support in the differential conversion range. It is conceivable that Ito et al. [14] performed their measurements in the range of catalytic ignition, whereas McCabe and Mitchell [16] operated in the differential range after ignition. However, neither working group differentiates between these ranges. Hermann [26] cannot find this difference either in his work using Pt/γ-Al_2O_3 catalysts. A comparison with the results of these studies is, however, of particular interest, since the experiments by Hermann were carried out in the same apparatus described in Section 2. However, Hermann did not use the SSTIs described in Chapter 2, but so-called plane expanded metal discs (PEMDs) with a geometrical surface of approximately 50 cm^2, onto which the Pt/γ-Al_2O_3 catalyst was applied. These PEMDs are the basis for the catalytic burners developed and currently used at Research Centre Jülich, which exhibit a Pt-particle density increased by a factor of 9 on the surface if compared with the SSTIs. Hermann [26] carried out his investigations at comparable space velocities. Fig. 2 shows that in comparison to the differential investigations in the SSTIs, a very low activation energy of 32.0 kJ/mol was found on the PEMDs. In the entire temperature range the rate constant of methanol oxidation on the PEMDs is lower by approximately a factor of 20 than in the SSTIs. This may be due to differences in catalyst preparation (dispersion of the metal) as well as improved mass and heat transfer properties in the SSTIs which are caused by a more turbulent gas flow. Table 1 summarizes the kinetic data and compares the effective reaction rates in the SSTIs with those on the PEMDs in the differential range of investigation and for conversions greater than 12% at two different reaction temperatures. In the differential range, the reaction rate in the SSTIs at a reaction temperature of 130°C is higher by a factor of 1.7 than on the PEMDs. At a reaction temperature of 170°C the factor is even 2.6. If the range with conversions greater than 12% is considered, the effective reaction rates in the SSTIs at 130°C are almost 10 times as high as those on the

Table 1
Kinetic parameters of the catalytic deep oxidation of methanol in Pt/γ-Al_2O_3 containing SSTI compared with literature, $T = 373$–$443\,K$, $c_{0\,MeOH} = 1345$–$2466\,ppm$, $m_{Pt} = 0.20$–$0.28\,mg$, $m_{Al_2O_3} = 2\,g$

Reaction zone	Parameter	Pasel et al.	Hermann [26]
Kinetics of the ignition	k_0 ($m^{3n}\,kg^{-1}\,s^{-1}\,mol^{-n+1}$)	2.895E + 10	–
	E_A (kJ/mol)	60.3	–
	n	0.5	–
Kinetics at $X < 12\%$	k_0 ($m^{3n}\,kg^{-1}\,s^{-1}\,mol^{-n+1}$)	4.691E + 09	2.233E + 06
	E_A (kJ/mol)	48.5	32.0
	n	1.4	0.4
Kinetics at $X > 12\%$	k_0 ($m^{3n}\,kg^{-1}\,s^{-1}\,mol^{-n+1}$)	3.153E + 06	2.233E + 06
	E_A (kJ/mol)	18.1	32.0
	n	1.4	0.4
$X < 12\%$, $T = 130°C$, $c = 2241\,ppm$	r_{eff} ($mol\,s^{-1}\,kg^{-1}$)	105.36	63.25
$X > 12\%$, $T = 130°C$, $c = 2241\,ppm$	r_{eff} ($mol\,s^{-1}\,kg^{-1}$)	629.68	63.25
$X < 12\%$, $T = 170°C$, $c = 2241\,ppm$	r_{eff} ($mol\,s^{-1}\,kg^{-1}$)	389.48	149.83
$X > 12\%$, $T = 170°C$, $c = 2241\,ppm$	r_{eff} ($mol\,s^{-1}\,kg^{-1}$)	1026.29	149.83

PEMDs, at 170°C the factor is 6.8. These values illustrate the large potential of SSTIs coated with catalysts. The amount of catalyst can almost be reduced 10 times depending on the reaction conditions so that the reactors for catalytic combustion, e.g., of the exhaust gases of a fuel cell can become markedly smaller and lighter and their dynamics can be improved.

3.2. *Pt/zeolite-coated SSTIs*

Fig. 3 shows the catalytic behaviour of the SSTIs from Fig. 1 coated with Pt/zeolite catalysts. In contrast to the results described above, in this case no independent kinetics can be discovered for the range of catalytic ignition. In the kinetically controlled range ($X < 10\%$) an activation energy of 30.4 kJ/mol is found, which compares very well with that of Hermann (32.6 kJ/mol) [26]. Great contrast is observed, however, in the reaction orders for methanol. Hermann [26] finds a reaction order of 0.5 for methanol on the PEMDs, whereas in the SSTIs of this study a strong dependence of the reaction rate on the methanol partial pressure with a reaction order of 1.7 was found in the differential range. In the entire temperature range, the rate constants of methanol oxidation in the SSTIs are higher by approximately a factor of 4 than on the PEMDs. In the case of the zeolite support, too, differences in catalyst preparation (dispersion of the metal) as well as improved mass and heat transfer properties in the SSTIs caused by a more turbulent gas flow may be an explanation. Non-differential conversions ($X > 10\%$) also lead to a limitation due to transport phenomena in the case of coating with Pt/zeolite. The apparent activation energy decreases to 13.1 kJ/mol and is less than half the value without inhibition due to mass transport. The reaction order for methanol is 1.3 and compares very well with the corresponding value found by measurements in the non-differential range using the Al_2O_3 support. Table 2 summarizes the kinetic data from Fig. 3 and compares the effective reaction rates in the SSTIs with those on the PEMDs in the two investigation ranges at two different reaction temperatures. Two opposite trends are observed. The low reaction order for methanol of 0.5 on the PEMDs has a more positive influence on the effective reaction rate in the concentration range investigated than the orders of 1.3 and 1.7 in the SSTIs, whereas the lower rate constants on the PEMDs have an adverse effect. In the range of differential conversions, the influence of the reaction order predominates so that clearly higher effective reaction rates are observed on the PEMDs compared to the SSTIs at 170 and 250°C. The factor is approximately 4–5. In the case of non-differential conversions, the higher rate constants dominate at 170°C, so that the reaction rate in the SSTIs is almost twice as high as on the PEMDs. At 250°C the opposite trends approximately cancel each other out. The results show that a coating of the SSTIs with Pt/zeolite catalysts is not meaningful, since better results can be obtained with this catalyst on the PEMDs.

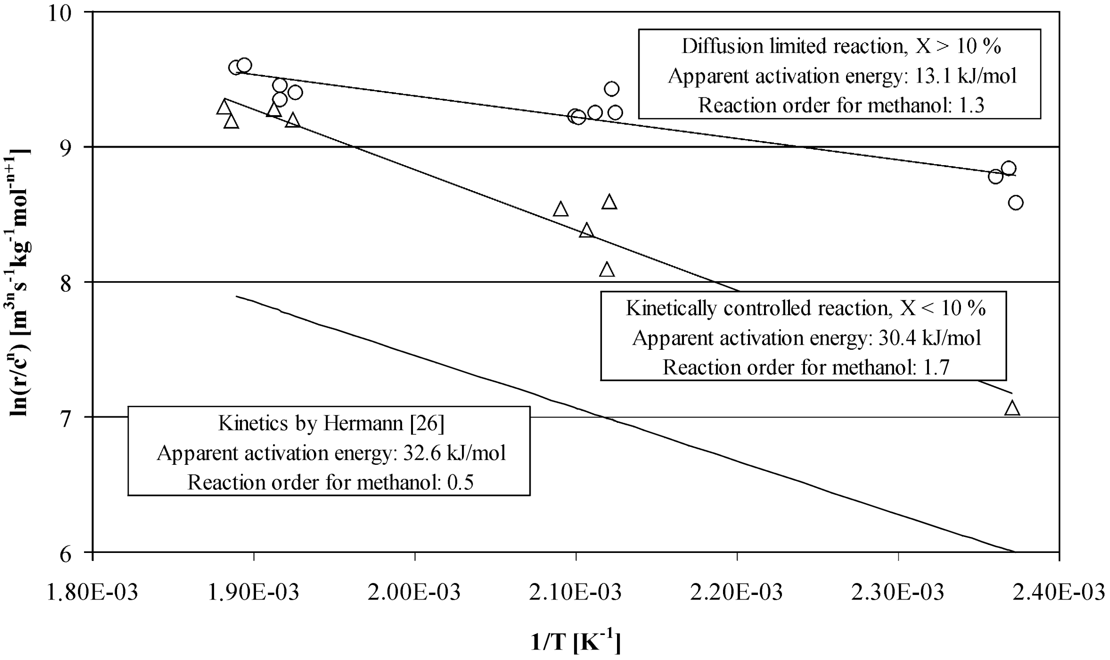

Fig. 3. Arrhenius plot for the catalytic deep oxidation of methanol in Pt/zeolite containing SSTI compared with literature, $T = 423$–$523\,\mathrm{K}$, $c_{0\,\mathrm{MeOH}} = 1793$–$3586\,\mathrm{ppm}$, $m_{\mathrm{Pt}} = 0.20$–$0.28\,\mathrm{mg}$, $m_{\mathrm{zeolite}} = 2\,\mathrm{g}$.

3.3. Comparison of Pt/γ-Al_2O_3- and Pt/zeolite-coated SSTIs

Fig. 4 compares the Pt/γ-Al_2O_3 and Pt/zeolite catalyst systems studied in this paper as catalytic coatings of the SSTIs from Fig. 1. In the range of differential conversions, comparable rate constants are achieved with these catalysts, but the temperature range in the case of coating with Pt/zeolite is approximately 60–90 K higher. In the range of non-differential conversions, the differences between the catalyst systems are more pronounced. The lowest rate constants achievable with the Pt/γ-Al_2O_3 catalyst at a reaction temperature of approximately 110°C are only slightly lower than the highest constants achieved with the Pt/zeolite contact at approximately 255°C. Both

Table 2
Kinetic parameters of the catalytic deep oxidation of methanol in Pt/zeolite containing SSTI compared with literature, $T = 423$–$523\,\mathrm{K}$, $c_{0\,\mathrm{MeOH}} = 1793$–$3586\,\mathrm{ppm}$, $m_{\mathrm{Pt}} = 0.20$–$0.28\,\mathrm{mg}$, $m_{\mathrm{zeolite}} = 2\,\mathrm{g}$

Reaction zone	Parameter	Pasel et al.	Hermann [26]
Kinetics at $X < 10\%$	k_0 ($\mathrm{m}^{3n}\,\mathrm{kg}^{-1}\,\mathrm{s}^{-1}\,\mathrm{mol}^{-n+1}$)	9.780E + 06	4.417 + 06
	E_A (kJ/mol)	30.4	32.6
	n	1.7	0.5
Kinetics at $X > 10\%$	k_0 ($\mathrm{m}^{3n}\,\mathrm{kg}^{-1}\,\mathrm{s}^{-1}\,\mathrm{mol}^{-n+1}$)	2.761E + 05	4.417E + 06
	E_A (kJ/mol)	13.1	32.6
	n	1.3	0.5
$X < 10\%$, $T = 170$°C, $c = 2241$ ppm	r_{eff} ($\mathrm{mol\,s}^{-1}\,\mathrm{kg}^{-1}$)	45.86	200.03
$X > 10\%$, $T = 170$°C, $c = 2241$ ppm	r_{eff} ($\mathrm{mol\,s}^{-1}\,\mathrm{kg}^{-1}$)	386.23	200.03
$X < 10\%$, $T = 250$°C, $c = 2241$ ppm	r_{eff} ($\mathrm{mol\,s}^{-1}\,\mathrm{kg}^{-1}$)	162.34	774.61
$X > 10\%$, $T = 250$°C, $c = 2241$ ppm	r_{eff} ($\mathrm{mol\,s}^{-1}\,\mathrm{kg}^{-1}$)	665.36	774.61

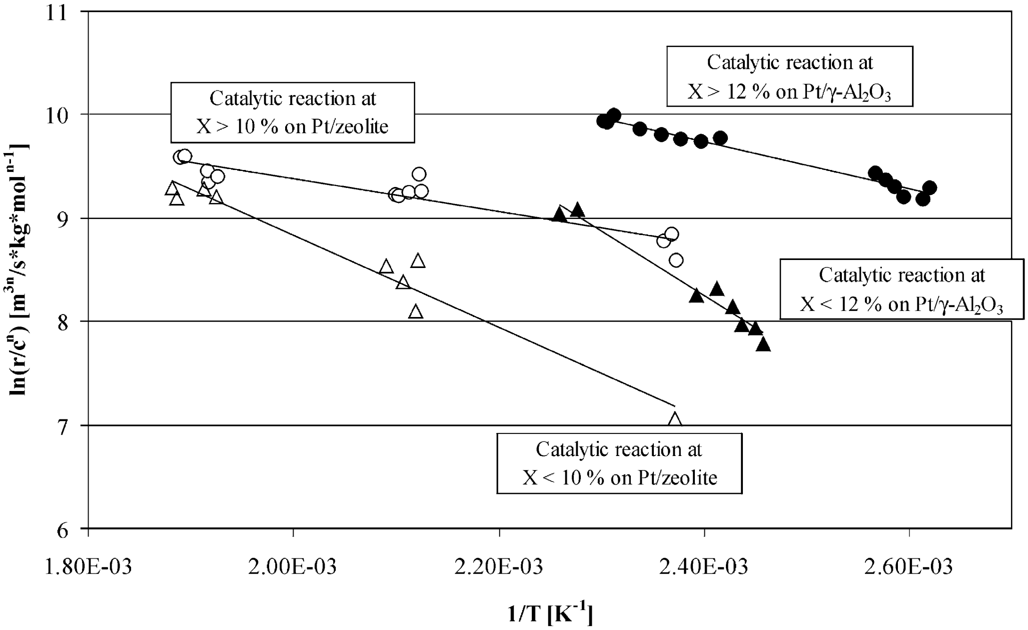

Fig. 4. Comparison of the Arrhenius plots for the catalytic deep oxidation of methanol in Pt/γ-Al_2O_3 and Pt/zeolite containing SSTI, reaction conditions as stated above.

catalyst systems have in common that the reaction orders for methanol are distinctly higher than 1 and exert an inhibiting influence on the effective reaction rates in the concentration range examined in comparison to lower reaction orders. In the non-differential range the activation energies are comparable for both catalysts and correspond in each case to less than half the activation energies in the differential range (cf. Tables 1 and 2), which is attributable to a strong limitation of the reaction process by mass transport phenomena. The effective reaction rates resulting from the kinetic parameters (cf. Tables 1 and 2) at a reaction temperature of 170°C are higher by a factor of 2.7 in the case of the Pt/γ-Al_2O_3 catalyst in the differential conversion range and even by a factor of 8.5 in the non-differential range than those of the Pt/zeolite contact. These results show that a Pt/γ-Al_2O_3 catalyst as the coating material is to be preferred to a Pt/zeolite contact, since the catalyst mass can be smaller by the factors specified.

4. Summary

SSTIs were constructed in which the kinetics of the catalytic deep oxidation of methanol was studied. For this purpose, the SSTIs were coated with two readily available catalyst materials, Pt/γ-Al_2O_3 and Pt/zeolite. The PEMDs so far used at Research Centre Jülich, in the so-called catalytic burner served for comparison. It was found that significantly higher reaction rates can be achieved in the SSTIs coated with Pt/γ-Al_2O_3 than on the PEMDs. This makes it possible to save a considerable amount of catalyst material. Based on the higher effective reaction rates and its spatial structure, this new development opens up prospects for a future smaller and lighter catalytic burner generation designed at Research Centre Jülich, which will also improve the dynamics of the catalytic burner. The SSTIs coated with Pt/zeolite do not offer these possibilities, since the effective reaction rates are lower than on the PEMDs.

References

[1] Esso Homepage.
[2] W. Wiese, B. Emonts, R. Peters, J. Power Sour. 84 (1999) 187–193.
[3] G. Veser, M. Ziauddin, L.D. Schmidt, Catal. Today 47 (1999) 219.

[4] G. Veser, L.D. Schmidt, AIChE J. 42 (1996) 1077.

[5] R.S. Drago, K. Jurczyk, D.J. Singh, V. Young, Appl. Catal. B 6 (2) (1995) 155.

[6] A.N. Pestryakov, A.A. Fyodorov, M.S. Gaisinovich, V.A. Shurov, I.V. Fyodorova, T.A. Gubaydulina, React. Kinet. Catal. Lett. 54 (1) (1995) 167.

[7] T. Seiyama, Catal. Rev.-Sci. Eng. 34 (4) (1992) 281.

[8] T. Nitadori, T. Ichiki, M. Misono, Bull. Soc. Chem. Jpn. 61 (1988) 621.

[9] A. Baiker, P.E. Marti, P. Kausch, E. Fritsch, A. Reller, J. Catal. 146 (1994) 268.

[10] G. Kremenic, J.M.L. Nieto, J.M.D. Tascón, L.G. Tejuca, J. Chem. Soc. Faraday 81 (1985) 939.

[11] T. Nakamura, N. Misono, Y. Yoneda, Chem. Lett. (1981) 1589.

[12] H.-B. Zhang, W. Wang, Z.-T. Xiong, G.-D. Lin, Stud. Surf. Sci. Catal. 130 (2000) 1547.

[13] A. Schwartz, L.L. Holbrook, H. Wise, J. Catal. 21 (1971) 199.

[14] K. Ito, B. Choi, O. Fujita, JSME Int. J. 33 (4) (1990) 778.

[15] L. Hiam, H. Wise, S. Chaikin, J. Catal. 10 (1968) 272.

[16] R.W. McCabe, P.J. Mitchell, Appl. Catal. 27 (1986) 83.

[17] A.A. Barresi, G. Baldi, Chem. Eng. Commun. 123 (1993) 31.

[18] R.W. McCabe, P.J. Mitchell, J. Catal. 103 (1987) 419.

[19] S.K. Agarwal, J.J. Spivey, J.B. Butt, Appl. Catal. 81 (2) (1992) 239.

[20] M.C. Marion, E. Garbowski, M. Primet, J. Chem. Soc., Faraday Trans. 86 (17) (1990) 3027.

[21] A.S.K. Sinha, V. Shankar, Chem. Eng. J. 52 (3) (1993) 115.

[22] F. Stolz, B. Schulz, K. Winkler, GDR Patent 280395 A1.

[23] Y. Michiue, Y. Fujiki, H. Tominaga, Chem. Lett. (1990) 2039.

[24] A. Ardhali Barani, D. Schmitt, M. Feger, H. Fueß, H. Klein, E.S. Lox, in: Proceedings of the XXXII Jahrestreffen Deutscher Katalytiker, March 17–19, 1999, Friedrichroda, Germany.

[25] M. Nagai, R.D. Gonzales, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 525.

[26] I. Hermann, Ph.D. Thesis, RWTH Aachen, Germany, 1998.