

Sizing of a Catalytic Reactor for Sulfuric Acid Reduction to Sulfur Dioxide Based on the Activation Parameters of $\text{SO}_3 \rightarrow \text{SO}_2$ Reaction

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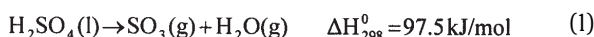
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The reduction of sulfuric acid to sulfur dioxide, a chemical process of industrial interest, needs catalyst and high temperature to proceed. In this work the activation parameters of the thermo-catalytic reduction of SO_3 to SO_2 in the presence of three commercial catalysts: 2 wt. % Pt/TiO_2 , 5 wt. % $\text{Pd/Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ were determined considering the first order dependence of the reduction reaction rate on SO_3 concentration in the gaseous mixture passing over the catalyst bed. Based on activation parameters the sizing of the catalytic reactor was performed. There are no big differences between dimensions of the catalyst beds, $\alpha\text{-Fe}_2\text{O}_3$ being advantaged because is cheaper and more available than Pd or Pt supported catalysts. When both the catalyst bed volume and mass are considered constant, the fractional conversion exponentially decreases with the mass flow rate of inlet sulfuric acid.

Keywords: sulfuric acid reduction, catalysts, activation parameters, reactor sizing

The thermo-catalytic reduction of sulfuric acid to sulfur dioxide is a chemical process of industrial interest, because it can be used to recycle the spent sulfuric acid, a very common by-product in chemical industry [1, 2]. In ^{15}N separation technology, by isotopic exchange in Nitrox system, the sulfur dioxide is used for nitric acid conversion into nitrogen oxides [3]. Important quantities of waste sulfuric acid, difficult to use because is diluted and contains solved sulfur dioxide, is produced in the same time. Sulfur dioxide recycling on a ^{15}N production plant, by reduction of sulfuric acid to sulfur dioxide, is one of the methods for diminishing of ^{15}N production costs. Also, the sulfuric acid reduction to sulfur dioxide is one of the most important energy consumption steps in all sulfur-based thermochemical cycles [4-6] for hydrogen production.

Sulfuric acid reduction takes place in two steps: the non-catalytic thermal decomposition of sulfuric acid to sulfur trioxide and water vapour, at temperatures around 400°C , followed by the thermo-catalytic reduction of sulfur trioxide to sulfur dioxide and oxygen at temperature above 750°C :



From both thermodynamic and kinetic point of view, high temperatures for SO_3 reduction are needed in order to achieve high chemical conversion degree, and a good energy efficiency of the process [7]. The SO_3 reduction shows a large kinetic barrier and, in order to reduce it, various catalysts are used [7, 8]; furthermore, the catalysts are also used to improve the reduction efficiency [9].

Reduction of sulfuric acid to sulfur dioxide has been studied since the '70, catalysts as: metal oxides, supported noble metals, or metal oxides and complex metal oxides being investigated. But numerous studies approached the problem only from the catalyst activity and stability point

of view. The kinetic measurements have been less approached, according to the experimental difficulties.

Spewock et al. [10] investigated the thermal catalytic reduction of SO_3 to SO_2 with two proprietary catalysts designated as WX-1 and WX-2, and determined the Arrhenius parameters of the reaction. The activation energy, in the case of first catalyst, was 227.61 kJ/mol and pre-exponential factor was $7.66 \cdot 10^{13} \text{ h}^{-1}$. The same parameters, in the case of second catalyst, were 73.05 kJ/mol and $2.45 \cdot 10^8 \text{ h}^{-1}$, its activity being proper for use in a compact decomposition reactor [10]. Comparing with recent data, Brown and Revankar [11] suggested that WX-2 is a platinum based catalyst.

Several oxides such as SiO_2 , Al_2O_3 , ZnO , CuO , NiO , Fe_2O_3 , MnO_2 , Cr_2O_3 , V_2O_5 and TiO_2 have been studied for the first time by Dokiya et al. [12] at temperatures of $800 - 870^\circ\text{C}$ and atmospheric pressure. Among these oxides, Fe_2O_3 was found to have the highest catalytic activity. Recent studies [13, 14] confirmed that iron (III) oxide has good catalytic activity. Giaconia et al. [14] studied the kinetics of SO_3 reduction on Fe_2O_3 catalyst and determined the Arrhenius parameters for Fe_2O_3 pellets of 2-6 mm diameter, respectively 1-2 mm diameter, at atmospheric pressure. The activation energies were 165.6 kJ/mol and 162.6 kJ/mol , respectively. The pre-exponential factors were $2.3 \cdot 10^8 \text{ h}^{-1}$ and $3.0 \cdot 10^8 \text{ h}^{-1}$, respectively.

Kinetic data for supported metal oxides, or noble metals, has been reported by Ishikawa et al., [15] who studied catalysts like $\text{Pt}(5\%) - \text{Al}_2\text{O}_3$, $\text{CuO}(5\%) - \text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3(5\%) - \text{Al}_2\text{O}_3$. For Pt catalyst the activation energy of 70.71 kJ/mol and the pre-exponential factor of $4.2 \cdot 10^7 \text{ h}^{-1}$ were determined. Ishikawa et al. [15] concluded that $\text{Pt} - \text{Al}_2\text{O}_3$ is the best catalyst, but $\text{CuO} - \text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3$ are promising catalysts because of their low cost and availability. Recently, Kondamudi and Upadhyayula [9] studied the reduction of sulfuric acid to sulfur dioxide with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ as catalyst and determined the activation energy for this reaction of 136.8 kJ/mol . The catalyst $\text{Pd/Al}_2\text{O}_3$ has been studied by Petropavlovskii et al. [16] and

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determined activation energy of 154 kJ/mol at 1000-1200 K and 0.1-3.0 MPa pressure.

In our previous work, [17] experimental research concerning sulfuric acid reduction to sulfur dioxide and oxygen in the presence of commercial catalysts: Pd/Al₂O₃, Pt/Al₂O₃ and α -Fe₂O₃ was performed in order to determine the catalytic activity and H₂SO₄ to SO₂ conversion degree for each catalyst. The good results obtained have strengthened the idea that the H₂SO₄ reduction process can be used for recycling of SO₂ on a ¹⁵N production plant.

Therefore, the research concerning H₂SO₄ reduction continued in this work with a kinetic study; the goal was to determine the activation parameters: activation energy and pre-exponential factor for catalytic reduction of SO₃ to SO₂ on three different catalysts: Pd/Al₂O₃, Pt/TiO₂ and α -Fe₂O₃. Based on this data and applying a simple method of calculation, the sizing of a reactor for catalytic reduction of sulfuric acid to sulfur dioxide is presented.

Experimental part

The kinetic studies were performed on the experimental plant presented in previous paper [17]. Concentrated sulfuric acid was fed by a peristaltic pump into tubular quartz reactor placed into an electric furnace. Once inside the heated zone, H₂SO₄ vaporized and decomposed to SO₃ and H₂O vapour, which pass over the catalyst bed, where SO₃ is reduced to SO₂. The catalyst is fixed inside the reactor between two beds of quartz beads (size between 1 and 4 mm) which are immobilized with the aid of quartz wool. The temperature was continuously measured in the middle of catalyst bed. The gaseous mixture, leaving the reactor, passes through a water-cooled condenser, where unreacted SO₃ reacts with water forming dilute sulfuric acid, which is collected into a trap, and SO₂, O₂ mixture was bubbled in 0.1 N NaOH solution for SO₂ absorption and oxygen was vented to hood. Collected sulfuric acid was determined by acid-base titration, using 0.1 N NaOH solution. Molar flow rate of SO₂ formed in reaction was determined by measuring the quantity of SO₂ absorbed into a known volume of 0.1 N NaOH solution.

The kinetic tests were performed with the following commercial catalysts: 5 wt. % Pd/Al₂O₃ (industrial catalyst produced in Russia), 2 wt. % Pt/TiO₂ (Johnson Mathey) and α -Fe₂O₃ (Alfa Aesar), in the temperature range of 750 - 900°C at atmospheric pressure. 96 wt. % H₂SO₄ was fed into reactor with a flow rate of 28 mL/h for Pd and Pt catalysts and 14 mL/h for α -Fe₂O₃. The H₂SO₄ flow rate in the case of α -Fe₂O₃ was only the half of the flow rate used for Pd and Pt supported catalysts, because α -Fe₂O₃ powder introduced an important pressure drop, even if it was mixed with quartz beads. The amount of catalyst loaded into reactor was 1 g. For each test fresh catalyst was used and the experiment time was 2 h.

Before loading into reactor, 5 wt. % Pd/Al₂O₃ catalyst pellets were crushed and sieved, granules with size between 0.4 and 0.8 mm being used in tests. 2 wt. % Pt/TiO₂ catalyst was used as spherical pellets, with size between 2 and 4 mm, and α -Fe₂O₃ as powder, mixed with quartz beads of 0.1 ÷ 0.3 mm. The crushing and sieving of 5 wt. % Pd/Al₂O₃ catalyst was possible because the relatively high palladium concentration (5 wt. %) makes that all pellets have practically the same Pd loading. The crushing of 2 wt. % Pt/TiO₂ was not possible according to the occurrence of pellets without metal and pellets that contain only metal so that the experimental conditions could not be reproduced. α -Fe₂O₃ powder was mixed with quartz beads in order to obtain a catalyst bed 2 cm length, as in the case of Pd and Pt catalysts.

Results and discussions

Activation parameters

Taking into account that the non-catalytic thermal decomposition of H₂SO₄ to SO₃ and H₂O vapour occurs faster than the thermo-catalytic reduction of SO₃, the overall process rate is given by the rate of sulfur trioxide reduction [18]. Therefore, it is considered that the first reaction is completed before SO₃ and water vapour pass over the catalyst bed, where the second reaction takes place.

Fractional conversion of SO₃ at different temperature, for all catalysts considered in this study, was determined from the ratio between the molar flow rate of SO₂ formed in reaction and the molar flow rate of concentrated sulfuric acid fed into reactor. In accordance with previous data [19-22], fractional conversion of SO₃ increases with temperature. The results are presented in figure 1.

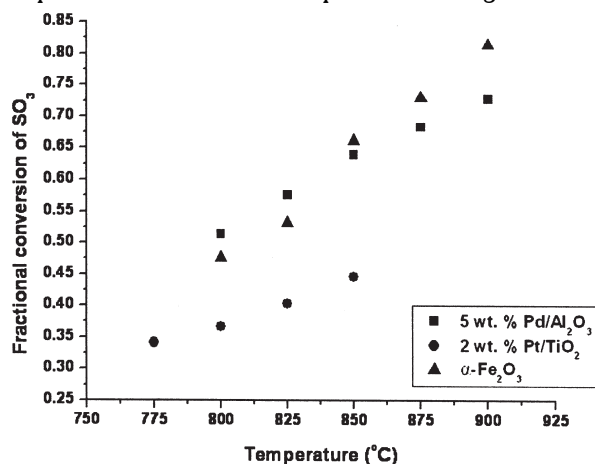


Fig. 1 The influence of temperature on fractional conversion of SO₃

Over 850°C, α -Fe₂O₃ catalyst shows higher SO₃ conversion than 5 wt. % Pd/Al₂O₃. Even if palladium based catalyst shows high fractional conversion, non noble metal catalyst should be considered from economical point of view. Therefore, iron oxide can be an alternative to noble metal based catalysts, taking into account its low cost and high availability.

In order to determine the activation energy and pre-exponential factor, for the SO₃ reduction to SO₂, a first order kinetic law is considered as suggested by Spewock et al. [10]

According to Giaconia et al. [14], the reaction rate constant (k) for SO₃ reduction to SO₂ can be expressed by the following equation:

$$k = -WHSV \cdot \ln(1 - X) \quad (3)$$

where: WHSV is the weight hourly space velocity (h⁻¹), defined as the ratio between the mass flow rate of inlet sulfuric acid and the mass of catalyst loaded into reactor and X is the fractional conversion of SO₃.

By substituting equation (3) in Arrhenius law expression:

$$k = A \cdot e^{-E_a/RT} \quad (4)$$

and applying logarithm on both sides, the following equation is obtained:

$$\ln[-\ln(1 - X)] = -\ln(WHSV/A) - E_a/RT \quad (5)$$

A plot of $\ln[-\ln(1 - X)]$ against $1/T$ for each catalyst (fig. 2) gives a straight line from which activation energy (E_a) and pre-exponential factor (A) were obtained. The results are presented in table 1.

The activation parameters for SO₃ reduction, using 2 wt. % Pt/TiO₂ catalyst, are not yet presented in the literature.

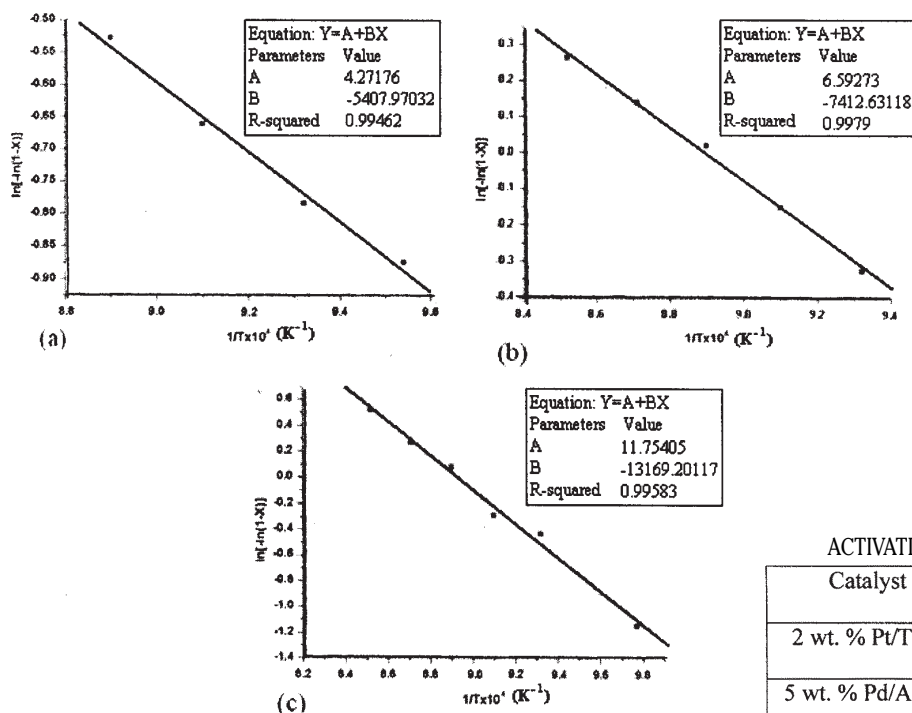


Fig. 2. Arrhenius plots for SO_3 reduction on: a) 2 wt. % Pt / TiO_2 ; b) 5 wt. % Pd / Al_2O_3 ; c) $\alpha\text{-Fe}_2\text{O}_3$

Table 1
ACTIVATION PARAMETERS FOR SO_3 REDUCTION

Catalyst	E_a (kJ/mol)	A (h^{-1})
2 wt. % Pt/ TiO_2	44.9 ± 3.3	3.5×10^3
5 wt. % Pd/ Al_2O_3	61.6 ± 2.3	3.6×10^4
$\alpha\text{-Fe}_2\text{O}_3$	109.4 ± 5.1	3.1×10^6

Catalyst	k (h^{-1})	W_{cat} (g)	WHSV (h^{-1})	V_R (cm^3)	$F_{\text{H}_2\text{SO}_4}^{\text{in}}$ (g/h)	ρ_{cat} (g/cm^3)	l (cm)	d (cm)
2 wt. % Pt/ TiO_2	28.51	1.037	47.79	1.25	49.46	0.83	1.59	1
5 wt. % Pd/ Al_2O_3	49.10	1.029	48.06	1.61	49.46	0.636	2	1
$\alpha\text{-Fe}_2\text{O}_3$	25.45	1.077	22.95	0.96	24.73	1.122	1.22	1

Table 2
THE REACTION RATE CONSTANT FOR SO_3 CATALYTIC REDUCTION AND OTHER EXPERIMENTAL PARAMETERS

Platinum on titania catalyst has been studied by Ginosar et al. [23, 24] but only in terms of catalytic activity and stability. The activation energy, that was obtained for SO_3 reduction on supported palladium catalyst, is much smaller than that reported by Petropavlovskii et al. [16]: 154 kJ/mol for a Pd/ Al_2O_3 catalyst, the amount of Pd and pre-exponential factor being not specified. The activation energy, obtained for SO_3 reduction catalyzed by iron oxide, is smaller than that reported by Giaconia et al. [14].

Reactor sizing

The calculation method for sulfuric acid reduction to SO_2 reactor sizing is relatively simple and can be applied for different catalysts.

Knowing the activation energy and pre-exponential factor for SO_3 reduction on a certain catalyst, the reaction rate constant has been calculated with Arrhenius equation (4). For the catalysts considered in our study, the reaction rate constants are presented in table 2.

Considering WHSV calculated from equation (3) and knowing the mass flow rate of inlet sulfuric acid ($F_{\text{H}_2\text{SO}_4}^{\text{in}}$), the catalyst mass (W_{cat}) can be obtained (table 2). The catalytic bed volume was calculated from relation:

$$V_R = \frac{W_{\text{cat}}}{\rho_{\text{cat}}} \quad (6)$$

From the ratio between the catalytic bed volume and surface area of the reactor cross section (0.785 cm^2), the

length (l) of the catalytic bed was determined. The total flow rate of the gaseous mixture entering the catalytic bed is 24.22 L/h ($\text{SO}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$) + $1.8 \text{ L/h He} = 26.02 \text{ L/h}$. The velocity in the free layer (v) of 9.2 cm/s was obtained from the ratio between the total flow rate of the gaseous mixture entering in the catalytic bed and surface area of the reactor cross section.

Considering a sulfuric acid 96 wt.% flow-rate of 4 mol/h , at catalytic bed temperature of 850°C and the velocity in the free layer of 9.2 cm/s , the length variation of reactor versus fractional conversion was achieved (table 3).

From these data can be observed that there are small differences between volumes and dimensions of the catalytic beds, which shows once again that the iron oxide can be an alternative to noble metal catalysts.

The catalytic bed dimensions dependence on the velocity in the free layer of the gaseous mixture passing the reduction reactor was also calculated. In table 4 are presented these results for studied catalysts, considering a sulfuric acid flow-rate of 4 mol/h , and the fractional conversion being constant for all velocities. The biggest catalyst bed volume is in the case of $\alpha\text{-Fe}_2\text{O}_3$ because the iron oxide powder was mixed with quartz pellets in order to diminish the pressure drop in the reduction reactor.

The variation of fractional conversion versus the mass flow rate of inlet sulfuric acid was calculated with relation:

Catalyst	X	WHSV (h ⁻¹)	V _R (cm ³)	W _{cat} (g)	l (cm)	d (cm)
2 wt. % Pt/TiO ₂	0.45	47.79	9.48	7.87	3.42	1.88
	0.5	41.22	11.0	9.13	3.96	1.88
	0.6	31.18	14.54	12.07	5.23	1.88
	0.7	23.73	19.10	15.85	6.87	1.88
	0.8	17.75	25.54	21.20	9.18	1.88
5 wt. % Pd/Al ₂ O ₃	0.64	48.06	12.29	7.83	4.42	1.88
	0.70	40.78	14.49	9.33	5.21	1.88
	0.75	35.42	16.67	10.62	5.99	1.88
	0.80	30.51	19.36	12.33	6.96	1.88
α-Fe ₂ O ₃	0.67	22.95	14.60	16.39	2.80	2.57
	0.70	21.40	15.66	17.58	3.01	2.57
	0.75	18.36	18.25	20.49	3.51	2.57
	0.80	15.81	21.20	23.80	4.08	2.57

Table 3
REACTOR LENGTH VERSUS FRACTIONAL
CONVERSION

Catalyst	X	V _R (cm ³)	v (cm/s)	l (cm)	d (cm)
2 wt. % Pt/TiO ₂	0.45	9.48	10	5.27	1.80
	0.45	9.48	8	4.74	2.02
	0.45	9.48	7	4.39	2.16
	0.45	9.48	6	4.07	2.33
5 wt. % Pd/Al ₂ O ₃	0.64	12.29	10	4.80	1.80
	0.64	12.29	9.2	4.42	1.88
	0.64	12.29	8.0	3.84	2.02
	0.64	12.29	7.0	3.66	2.16
	0.64	12.29	6.0	2.87	2.33
α-Fe ₂ O ₃	0.67	14.60	10	8.11	1.80
	0.67	14.60	8	7.23	2.02
	0.67	14.60	7	6.76	2.16
	0.67	14.60	6	6.27	2.33

Table 4
DEPENDENCE OF THE CATALYTIC BED DIMENSION ON
THE VELOCITY IN THE FREE LAYER

$$-\ln(1-X) = \frac{A \cdot e^{-E_a/RT}}{F_{H_2SO_4}^m} \cdot V_R \cdot \rho_{cat} \quad (7)$$

The results are presented in figure 3. It can be seen that the fractional conversion exponentially decrease with the mass flow rate of inlet sulfuric acid, when both catalyst bed volume and mass are constant.

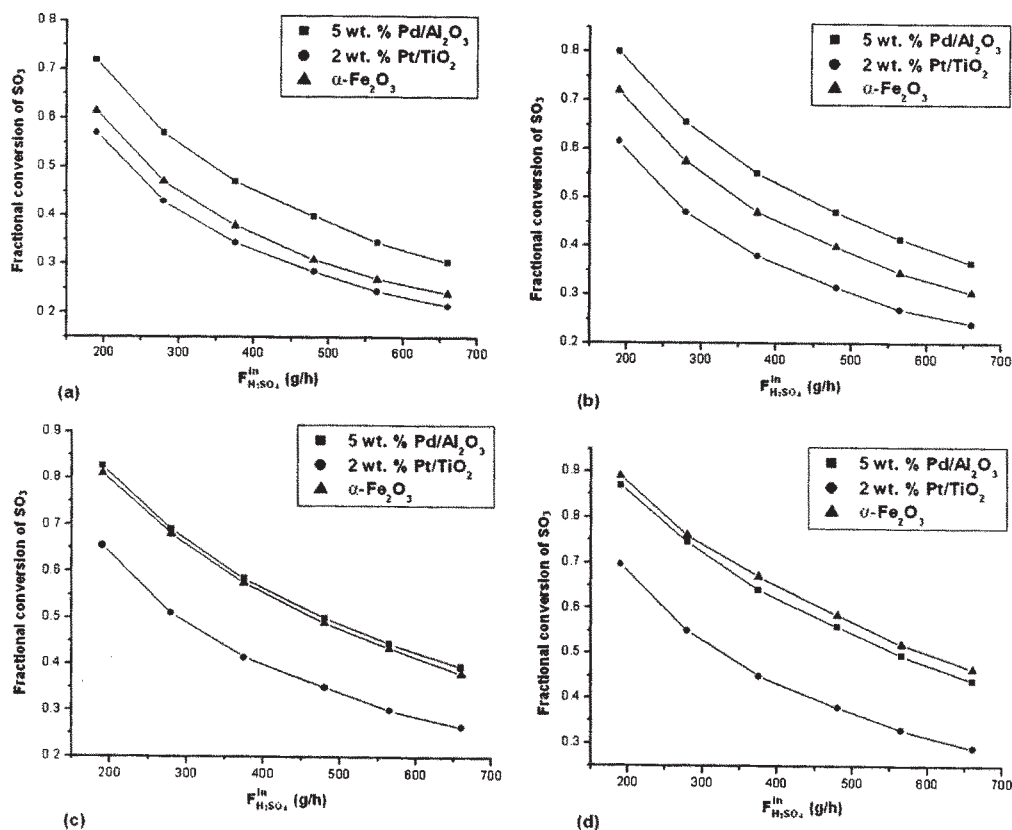


Fig. 3. Fractional conversion of SO_3 vs. mass flow rate of inlet sulfuric acid: a) 775°C; b) 800°C; c) 825°C; d) 850°C

Conclusions

In this work three different catalysts: 2 wt. % Pt/TiO_2 , 5 wt. % $\text{Pd/Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$, have been tested in the kinetic studies of SO_3 reduction to SO_2 in the temperature range 750 - 900°C and atmospheric pressure. At temperature equal or above 850°C, iron oxide could be considered a better catalyst, because it leads to high conversions and has a low cost, therefore, it can be an alternative to noble metal based catalysts.

Considering a first order kinetic for the SO_3 reduction, the Arrhenius parameters were determined. The activation energy for SO_3 reduction is: 44.9 kJ/mol for Pt/TiO_2 , 61.6 kJ/mol for $\text{Pd/Al}_2\text{O}_3$ and 109.4 kJ/mol for Fe_2O_3 . The values obtained for Pd and iron oxide catalysts are smaller than those presented in literature for the same type catalysts.

A method for the sizing of a reactor for catalytic reduction of sulfuric acid to sulfur dioxide is presented. The reactor sizing starts from the experimentally determined activation parameters. Using these kinetic parameters, the reaction rate constants and the weight hourly space velocity (WHSV) were determined. There were not found big differences between the volumes and dimensions of the studied catalytic beds, therefore iron oxide being advantaged to noble metal based catalysts. The fractional conversion of sulfuric acid to sulfur dioxide exponentially decreases with the mass flow rate of inlet sulfuric acid, when both the bed volume and the catalyst mass are constant.

This method for sizing of reactor for sulfuric acid reduction to sulfur dioxide can provide a guideline for designers to achieve a large fractional conversion with an economical design.

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