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Kinetic Modelling for the Dehydration of Methanol to Dimethyl Ether over γ-Al_2O_3

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A kinetic model has been established for the dehydration of methanol to dimethyl ether over γ-Al_2O_3 acid function, the most widely used catalyst. The kinetic model considers the reaction of methanol dehydration to be elementary. The effect of water in the reaction medium (due to the high adsorption capacity of γ-Al_2O_3) has been considered by adding a term to the reaction rate expression, which takes into account the partial inhibition of active site activity. Thirteen different models have been tested. The simplest one does not take into account the effect of water on reaction kinetics; six models consider an exponential effect of water in the term of attenuation of reaction kinetics, and a further six models consider a hyperbolic effect. The selection of the best model has been carried out on the basis of the Fisher test. The model which best fits the experimental data is the one that considers an exponential effect of water, methanol and dimethyl ether.

1. Introduction

The synthesis of dimethyl ether (DME) has received considerable attention in the literature, because of its potential use as a multipurpose fuel. Another reason is that it can be produced from a variety of resources, such as natural gas, coal and biomass, which contributes to reducing the energy dependence on oil (Semelsberger, 2006). DME can be used either as a gasoline additive, or directly as an automotive fuel alternative to diesel fuel (Arcoumanis et al., 2008). Moreover, DME is a strategic raw material which could replace methanol in the production of hydrocarbons (such as light olefins and BTXE) and chemicals (dimethyl sulphate, methyl acetate). In addition, it is suitable to be used as an aerosol propellant as a green substitute for CFCs, which were banned because they cause the depletion of the ozone layer (Fleisch et al., 2012).

The catalytic dehydration of methanol over solid-acid catalysts is a suitable process for DME synthesis, which is the previous stage in the transformation of methanol into hydrocarbons (MTG process) or olefins (MTO process). Another possibility is the synthesis of DME from synthesis gas in one reaction step over bifunctional catalysts, process in which methanol dehydration is essential to shift the thermodynamic equilibrium of methanol synthesis (Ereña et al., 2005). In both processes, the selective production of DME is mainly related to active sites of weak and medium acidity, being γ-Al_2O_3 the most commonly used acid function.

The kinetics of the selective dehydration of methanol to DME has been extensively studied in the literature. Some authors have proposed either the dissociative adsorption of methanol (Figueras et al., 1971; Klusaček and Schneider, 1982; Bercic and Levec, 1992) or the molecular adsorption (Gates and Johanson, 1971) as the controlling step. Nevertheless, most of the kinetic models proposed were derived from experiments conducted in conditions not found in an industrial reactor (where methanol dehydration reaction takes place at high conversion levels), or over catalysts with a low stability and reproducibility. Furthermore, the water produced during the dehydration of methanol considerably lowers the reaction rate, and the kinetic models do not take into account this effect.

The presence of water in the reaction medium has a considerable unfavourable effect, as it causes a decrease in the equilibrium values of DME yield and selectivity. Moreover, it may have several negative effects on the catalyst, such as i) the attenuation of the activity of the acid function, due to its adsorption on active sites and ii) the partial dealumination of the catalyst, due to the presence of vapour at high temperature, which is important in HZSM-5 zeolite above 400 ºC and leads to irreversible deactivation by the loss of Al in zeolite framework (Gayubo et al., 2004).

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Many authors (Xu et al., 1997; Akarmazyan et al., 2012) have reported the poisoning effect of water on the catalytic activity of γ-Al_2O_3 for the synthesis of DME from methanol. Water molecules seem to occupy the acid sites of the catalyst and prevent methanol from being adsorbed on these sites. Moreover, Lewis acid-sites might be changed to Brönsted acid-sites in the presence of water. Similar results have been obtained in the synthesis of DME from mixtures of (H_2+CO) in one reaction step using a CuO-ZnO-Al_2O_3/γ-Al_2O_3 bifunctional catalyst (Aguayo et al., 2005), and consequently, it is advisable to configure the catalyst with an excess of the acid function (Sierra et al., 2010a). This aspect becomes even more important when using the strategy of co-feeding water to attenuate catalyst deactivation by coke (Sierra et al., 2011).

The aim of this work is the development of a kinetic model for the dehydration of methanol to DME over γ-Al_2O_3 acid function, which rigorously considers the inhibiting effect of water on reaction kinetics.

2. Experimental

γ-Al_2O_3 acid function has been prepared by the coprecipitation of a $NaAlO_2$ suspension with HCl at 70 ºC until the pH reaches a value of 9.0. The following steps are the aging of the catalyst at 70 ºC for 1 h, filtering, washing, drying (at 20 ºC and at 120 ºC for 12 h each), and calcination (550 ºC, 2 h).

The experimental equipment used, Autoclave Engineers BTRS Jr., is provided with a fixed bed. On-line product analysis has been carried out by means of an Agilent 6890 gas chromatograph, provided with FID and TCD detectors. Experimental data have been collected in a wide range of operating conditions: $(1.5\text{-}40)\cdot 10^5$ Pa; 150-450 ºC; space time, 0.005-1.0 (g of catalyst) h (g of methanol)$^{-1}$. The attenuating effect of water in the reaction medium has been studied using different mixtures of methanol and water in the feed (molar fraction of water= 0, 0.2, 0.4, 0.6 and 0.8).

3. Kinetic modelling and parameter estimation

The method used to calculate the kinetic parameters is based on solving the mass conservation equation for each component, on the assumption of plug flow and isothermal operation. The kinetic model considers the following reaction rate equation, which is based on the assumption of elementary reaction:

$$r_{DME}=k\left(P_{MeOH}^{2}-\frac{P_{DME}\cdot P_{H_2O}}{K}\right)\theta \tag{1}$$

where r_{DME} has been defined as the moles of DME formed per unit mass of catalyst and unit time; P_i is the partial pressure of i component; and k and K are the kinetic and equilibrium constants, respectively.

A term θ has been included to quantify the attenuating effect of the adsorption of the reaction products (mainly water, due to its high adsorption capacity, but also methanol and DME). This effect has been taken into account in previous papers, in the kinetic models established for the synthesis of DME in one reaction step from syngas and CO_2 (Sierra et al., 2010b; Ereña et al., 2011).

The equilibrium constant for the dehydration of methanol to DME has been related to temperature (K) by means of the following expression (Aguayo et al., 2007).

$$K=\exp\left(-9.76+\frac{3.20\,10^{3}}{T}+1.07\,\log T-6.57\,10^{-4}T+4.90\,10^{-8}T^{2}+\frac{6.05\,10^{3}}{T^{2}}\right) \tag{2}$$

The kinetic models tested are listed in Table 1. These models consider alternative expressions for the adsorption term θ (Equation (1)). The simplest model (Model 0) does not take into account the effect of water on methanol dehydration kinetics. Two different effects of water have been tested, exponential and hyperbolic. For each effect six kinetic models have been proposed, with increasing complexity. Several models also consider the possibility of the other reaction products (methanol and DME) being adsorbed on the acid sites of γ-Al_2O_3. P_i is the partial pressure of i component, K_i is a term that quantifies the capacity for the adsorption of i component, and n, m, q and x are kinetic parameters of fitting.

The conversion of methanol (X_{MeOH}) has been defined as:

$$X_{MeOH}=\frac{n_{MeOH,0}-n_{MeOH}}{n_{MeOH,0}}\cdot 100 \tag{3}$$

where $n_{MeOH,0}$ and n_{MeOH} are the molar flow rates of methanol in the reactor inlet and outlet stream, respectively. The experimental results of X_{MeOH} are not affected by catalyst deactivation, which is very slow under the operating conditions used.

The calculation of kinetic parameters has been performed by fitting the experimental values of methanol conversion to the mass conservation equations, using a program written in MATLAB. The kinetic parameters which provide the best fit have been determined by multivariable non-linear regression, using the Marquardt method. The overall objective function to be minimized takes into account the deviations between the experimental and calculated values of methanol conversion.

Table 1: Expressions for the term of attenuation of catalyst activity (θ) for each model.

Model	Θ	Equation No.
0	1	(4)
	Exponential effect	
1	$e^{-K_{H_2O}\cdot P_{H_2O}}$	(5)
2	$e^{-K_{H_2O}\cdot P_{H_2O}^{n}}$	(6)
3	$e^{-K_{H_2O}\cdot P_{H_2O}^{n}}\cdot e^{-K_{MeOH}\cdot P_{MeOH}}$	(7)
4	$e^{-K_{H_2O}\cdot P_{H_2O}^{n}}\cdot e^{-K_{MeOH}\cdot P_{MeOH}^{m}}$	(8)
5	$e^{-K_{H_2O}\cdot P_{H_2O}^{n}}\cdot e^{-K_{MeOH}\cdot P_{MeOH}^{m}}\cdot e^{-K_{DME}\cdot P_{DME}}$	(9)
6	$e^{-K_{H_2O}\cdot P_{H_2O}^{n}}\cdot e^{-K_{MeOH}\cdot P_{MeOH}^{m}}\cdot e^{-K_{DME}\cdot P_{DME}^{q}}$	(10)
	Hyperbolic effect	
7	$\frac{1}{1+K_{H_2O}\cdot P_{H_2O}^{n}}$	(11)
8	$\frac{1}{1+K_{H_2O}\cdot P_{H_2O}^{n}+K_{MeOH}\cdot P_{MeOH}}$	(12)
9	$\frac{1}{1+K_{H_2O}\cdot P_{H_2O}^{n}+K_{MeOH}\cdot P_{MeOH}^{m}}$	(13)
10	$\frac{1}{1+K_{H_2O}\cdot P_{H_2O}^{n}+K_{MeOH}\cdot P_{MeOH}^{m}+K_{DME}\cdot P_{DME}}$	(14)
11	$\frac{1}{1+K_{H_2O}\cdot P_{H_2O}^{n}+K_{MeOH}\cdot P_{MeOH}^{m}+K_{DME}\cdot P_{DME}^{q}}$	(15)
12	$\frac{1}{\left(1+K_{H_2O}\cdot P_{H_2O}^{n}+K_{MeOH}\cdot P_{MeOH}^{m}+K_{DME}\cdot P_{DME}^{q}\right)^{x}}$	(16)

In order to reduce the correlation between the estimated values of frequency factor and activation energy (both parameters are related by means of the Arrhenius equation), a reparametrization has been used, in such a way that the initial estimation of the reaction parameters is less critical and the time required for the program to reach the minimum value of the objective function is lower. According to this reparametrization, the kinetic constant is redefined as:

$$k = k^{*}\exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right] \tag{17}$$

where E_a is the activation energy and T* is a reference temperature (300 ºC).
The constant K_i, related to the adsorption capacity of i component, also depends on temperature, according to the following reparametrized equation:

$$K_i = K_i^{*}\exp\left[\frac{\Delta H_i}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right] \tag{18}$$

Given that the expressions for θ (Equations (5)-(16)) are empirical, the relationship between ΔH_i and the adsorption enthalpies is not straightforward, although both parameters are related.

The discrimination of the kinetic models has been carried out on the basis of the statistics calculated for the F distribution. The selected procedure is the stepwise regression, which is based on introducing new parameters and testing the significance of the added parameters, by means of the comparison of F and F_c functions. The critical function F_c can be obtained from the Fisher table (a confidence level of 95 % has been selected).
The value of the F statistics to decide if the addition of new parameters from Model a to Model b is significant is $F_{a\text{-}b}$. The procedure is based on the comparison of the values of $F_{a\text{-}b}$ and F_c for each addition of new fitting parameters. If the value of $F_{a\text{-}b}$ function is higher than the critical value F_c, this means that the improvement due to the addition of new parameters is significant. In this case, the most complex model, model b, must be selected. On the contrary, if the value of $F_{a\text{-}b}$ is lower than the critical value F_c, the improvement in the fitting is not significant and the simplest model, model a, must be selected. The discrimination performed using the F test has allowed us to select two models, one with an exponential term and another with a hyperbolic term.

4. Results

Figure 1 shows, as an example, the poor fitting of the experimental values of methanol conversion to the model proposed by Bercic and Levec (1992). It has also been observed the poor fitting of the data obtained in this work to the other models in the literature since these models: i) have been developed using the data of experiments in which the conversion of methanol is low, and with catalysts and operating conditions different to those used in this work; ii) do not consider the role of water in the attenuation of reaction rate.
The kinetic data of methanol dehydration have been collected and fitted to Equation (1), using the proposed terms of adsorption (θ) of Table 1, Equations (4)-(16). Table 2 shows the results of the application of the Fisher test to the six models which consider an exponential term. It is observed that the model of best fitting is Model 6.

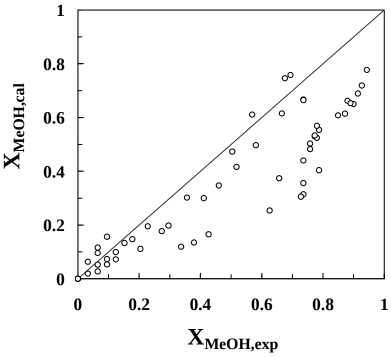

Figure 1: Fitting of experimental data of methanol conversion to the model of Bercic and Levec (1992).

Table 2: Comparison of $F_{a\text{-}b}$ and F_c values for the models which consider an exponential effect of the adsorbed components.

Models compared	0-1	1-2	2-3	3-4	3-5	5-6
$F_{a\text{-}b}$	1.5657	1.3171	7.1388	0.9716	1.6252	1.3715
F_c	1.1838	1.1842	1.1846	1.1850	1.1853	1.1858
Selected model	1	2	3	3	5	6

Table 3 lists the results of the application of the F test to the models which consider a hyperbolic effect of water. As for the models which consider an exponential effect, the selected model is also the most complex of the models tested, Model 12.

Table 3: Comparison of $F_{a\text{-}b}$ and F_c values for the models which consider a hyperbolic effect of the adsorbed components.

Models compared	0-7	7-8	8-9	9-10	10-11	11-12
$F_{a\text{-}b}$	2.0825	1.3756	2.4342	1.8976	1.2113	1.2102
F_c	1.1840	1.1846	1.1850	1.1854	1.1858	1.1861
Selected model	7	8	9	10	11	12

Finally, the discrimination between the chosen models has been carried out, using the same procedure. The results of the application of Fisher test for these two models are listed in Table 4. It is concluded that the most suitable model is Model 6, which considers an exponential effect of water, methanol and DME:

$$r_{DME} = k\left(P_{MeOH}{}^{2} - \frac{P_{DME} \cdot P_{H_2O}}{K} \right) e^{-K_{H_2O} \cdot P_{H_2O}{}^{n}} \cdot e^{-K_{MeOH} P_{MeOH}{}^{m}} \cdot e^{-K_{DME} \cdot P_{DME}{}^{q}} \qquad (19)$$

Table 4: Comparison of F statistics values for the models of best fitting.

Models compared	6-12
F_{a-b}	0.4119
F_c	1.1861
Selected model	6

Figure 2 shows the experimental and calculated data of methanol conversion for the model of best fit (Model 6). Model 6 provides a reasonable fit in the whole range of methanol conversion. Figure 3 shows the comparison between experimentally measured and estimated values of methanol conversion for different temperatures. The results correspond to the following operating conditions: 250-400 ºC; $1.5 \cdot 10^5$ Pa; space time, 0.88 (g of catalyst) h (g of feed)$^{-1}$; molar fraction of water in the feed, 0.8. It is observed that Model 6 provides a suitable fitting, especially for low values of methanol conversion. The deviation between measured and calculated data increases for values of conversion higher than 0.6. In Table 5 the values of the error objective function, the residual variance and the main kinetic parameters for the model of best fitting (Model 6) are shown. The values of the kinetic parameters have been obtained for a reference temperature of 300 ºC.

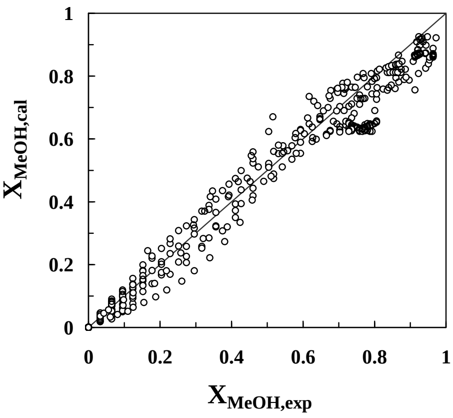

Figure 2: Fitting of experimental data of methanol conversion to Model 6.

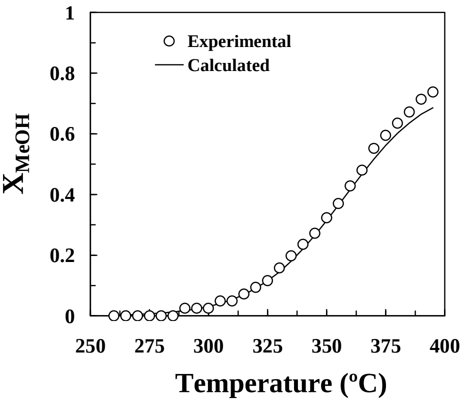

Figure 3: Comparison between measured and estimated values of methanol conversion for one series of experiments.

Table 5: Values of the kinetic and statistical parameters for Model 6.

Kinetic and statistical parameters	Value
k, mol·$g_{catal.}^{-1}$·h^{-1}·Pa^{-2}	$2.64 \cdot 10^{-7}$
E_a, kJ·mol^{-1}	263.6
K_{H2O}*, $Pa^{-0.36}$	0.171
ΔH_{H2O}, kJ·mol^{-1}	3.60
K_{MeOH}*, $Pa^{-1.86}$	$1.68 \cdot 10^{-9}$
ΔH_{MeOH}, kJ·mol^{-1}	2.01
K_{DME}*, $Pa^{-0.86}$	$3.47 \cdot 10^{-4}$
ΔH_{DME}, kJ·mol^{-1}	7.20
N	0.36
M	1.86
Q	0.86
Overall objective function (Φ)	0.039
Variance (σ^2)	0.0049

5. Conclusions

Thirteen kinetic models for the dehydration of methanol to DME have been tested. These models take into account the role of water in the reaction medium, given that it has a relevant effect as an inhibitor of reaction rate. The model which best fits the experimental data of methanol conversion has an exponential term of attenuation and considers the competitive adsorption of water, methanol and DME. This model suitably fits the concentrations of the individual components in the reaction medium in a wide range of experimental conditions: $1.5\text{-}40\cdot10^5$ Pa; 150-450 ºC; space time, 0.005-1.0 (g of catalyst) h (g of methanol)$^{-1}$; molar fraction of water in the feed, 0-0.8.

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