Study of HMS Modified ZrO$_2$ Supported Platinum Catalysts for Toluene Removal: Catalytic Combustion and Kinetics Study

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Reaction behaviors and kinetics of catalytic oxidation of toluene with different feed flows over Pt/Zr(x)-HMS catalysts with Si/Zr ratio equal to 5, 10, 20 and 35 were investigated over a wide temperature range (200-500 °C). Results show that Pt/Zr(x)-HMS has the best catalytic performance. The kinetics data were fitted by the Power-law and Mars-van Krevelen kinetics models. The fitting results show that the Mars-van Krevelen model ($R^2 > 0.99$) is more suitable for predicting the conversion of toluene than the Power law model ($R^2 = 0.53$), and the Mars-van Krevelen model can accurately express the reaction rate of this process.

INTRODUCTION

Following a warning increase in volatile organic compounds (VOCs) and their harmful effects on the environment and human health, the deep oxidation by Pt catalysts has been adopted as one of the most widely methods to eliminate these compounds. Many efforts have been made in this regard for the design of effective catalysts [1-5]. Supported noble metals or transition metal oxides are among the most widely used catalysts for this process [6,7]. It is well documented that the support plays a determinant role in improving the supported noble metals catalysts' activity. The choice of catalyst support usually depends on its specific surface area, pore size and the capacity for interaction with metals [7].

Transition metal oxides have a very low surface area despite good results in this reaction. It seems that the use of surface enhancement techniques for the production of these catalysts will improve their performance [8].

Developing new and more efficient catalysts for reducing the emission of VOCs, particularly/mainly

benzene derivatives, has been urgently demanded. Accordingly, we used zirconium metal oxide, and in order to increase its surface area, we combined this metal oxide with hexagonal mesoporous silica (HMS) as composite support [9].

In our previous work [9], the ZrO$_2$ modified hierarchical porous silica (HMS) with mesoporous structure was successfully synthesized *via* a reported method [9] and used as the support of active component Pt species. These catalysts were completely characterized and investigated for n-heptane reforming. The results show that this catalyst has a good catalytic performance.

Herein, Pt/ZrO$_2$-HMS was used to develop new catalytic formulations in elimination of VOCs. In this respect, the role of Si/Zr ratio on catalytic properties and kinetics for oxidation of toluene has been deeply investigated.

EXPERIMENTAL TECHNIQUES

Catalyst Preparation and Characterization Methods

Details of the used materials, synthesis procedure and

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characterization techniques have been completely described elsewhere [9]. Briefly, after adding of zirconyl nitrate to the appropriate amounts of tetraethyl ortho silicate and dodecyl amine, the obtained solid materials were filtered, calcined and impregnated by platinum (0.6 wt%). These catalysts were named as Pt/Zr(x)-HMS that x is Si/Zr ratio and equal to 5, 10, 20 and 35.

X-ray fluorescence (XRF), X-ray diffraction (XRD) patterns, H_2 chemisorption, Fourier transform infrared (FT-IR), N_2 adsorption-desorption isotherms, temperature programmed desorption of NH_3 (NH_3-TPD), Fourier transform infrared of pyridine (Py-IR), field emission scanning electron microscope (FESEM) and thermogravimetric/differential thermal analysis (TG/DTA) were used to analyze catalysts that details of these analytical methods have been reported elsewhere [9].

Catalytic Evaluation

Activity testing. Catalytic tests were run over each Pt/Zr(x)-HMS catalyst, placed inside a quartz fixed bed flow reactor. Before the reaction, each catalyst (0.3 g) was subjected to a pretreatment at 400 °C for 2 h under He stream. The experimental setup consisted of a mass flow controller for dry air, a bottle filled with liquid toluene, a furnace, a quartz reactor, and a gas analyzer (Delta 1600-L) system. In the case of toluene oxidation, the activity was measured at atmospheric pressure between 200 and 500 °C, with a feedstock of air (3 ml s^{-1} flow rate) and toluene (2 ml h^{-1} flow rate). The only primary obtained products were toluene (Tu), H_2O, CO and CO_2. Other products were not detected under our experimental conditions.

Stability tests in the case of prepared catalysts were also performed for toluene oxidation with the same reactant mixture as mentioned above, at 350 °C for 60 h.

Mass transfer limitations. Since the kinetics experiments should be carried out in the absence of mass transfer, diffusion limitations were examined prior to kinetics testing of toluene oxidation at 200 to 500 °C. First of all, effect of the external transport of toluene was evaluated by comparing the conversion profiles of a set of experiments where only the catalysts' weight was varied from 0.1 to 0.5 g. The height of the catalytic bed

was maintained constant by the addition of inert quartz. The quartz was used to dilute the catalyst due to its ineffectiveness on the catalytic conversion.

Subsequently, the effect of the internal transport was evaluated by running a set of experiments with the catalyst particles having different mean particle size (50-350 μm) while the other conditions were kept the same.

Kinetics experiments. To further evaluate the differences in the catalytic ability, kinetics study of toluene oxidation was performed over the prepared catalysts at the following conditions: 200-500 °C temperature range, a varied flow rate of gaseous toluene from 1.5 to 3 ml h^{-1} and a varied O_2 flow rate of 12.6-50.4 ml min^{-1}.

The Power law and Mars-van Krevelen kinetics models were applied in the case of toluene oxidation with the conversion less than 10%.

Power law (PL) model. This model was chosen as a simple and useful kinetics equation for preliminary design or comparison.

$$w \left(\frac{mol}{g \, s} \right) = k P_{O2}^n P_{Tu}^m \tag{1}$$

where w: reaction rate (mol g^{-1} s^{-1}); k: rate constant; P_{o2} partial pressure of oxygen (Pa); P_{Tu} partial pressure of toluene (Pa); n and m: rate exponents of the reaction.

The rate constant (k) follows Arrhenius equation;

$$k = A e^{\frac{E_{app}^{act}}{RT}} \tag{2}$$

where $\frac{E_{app}^{act}}{RT}$: apparent activation energy (kJ mol^{-1}); R: gas constant (kJ mol^{-1} K^{-1}); A: pre-exponential factor, and T reaction temperature (K). The adjustment procedure is obtained by solving Eqs. (1) and (2) using the obtained experimental data.

The reaction rate was calculated by the following equation:

$$w \left(\frac{mol}{g \, s} \right) = \frac{Tu \; flow \, rate \times Tu \, density \times conversion \, (\%)}{Tu \, molar \, weight \times weight \, of \, catalyst \times impregnated \, metal} \tag{3}$$

The PL model was used to determine the exponents of O$_2$ and Tu in the toluene oxidation process. For measuring the toluene exponent (m), the catalysts were investigated at 200-500 °C containing 1.5 to 3.0 ml h^{-1} flow rate of toluene whereas the O$_2$ flow rate at 180 ml min^{-1} was kept constant. After each reaction, catalysts were cleaned in a flow of He while heating at 400 °C before cooling to 200 °C and continuing the other step of reaction. The similar procedure was employed to obtain the O$_2$ exponent (n). On this basis, the flow rate of O$_2$ was changed between 60 and 240 ml min^{-1} while maintaining the toluene at 2 ml h^{-1} flow rate. After each experiment, reaction mixtures were analyzed by a gas analyzer at a fixed interval of time (1 h). Other kinetic parameters for these equations were calculated using the experimental data obtained from the experiments.

Mars-van Krevelen (MVK) model. This model assumes two steps in the oxidation of toluene. The first step includes the reaction of adsorbed toluene with the oxygen on the catalyst. Therefore, in this step, the metal oxide of catalyst is reduced. In the second step, the reduced metal oxide is re-oxidized by oxygen [10]. According to this mechanism, the rate of toluene oxidation can be expressed by Eq. (4).

$$w = \frac{k_{O2} k_{Tu} P_{O2} P_{Tu}}{\gamma k_{Tu} P_{Tu} + k_{O2} P_{O2}} \qquad (4)$$

where, w: reaction rate (mol g^{-1} s^{-1}); P$_{Tu}$ partial pressure of toluene; P$_{O2}$ partial pressure of oxygen (Pa); k$_{Tu}$ rate constant of toluene oxidation (Pa); k$_{O2}$ rate constant of catalyst re-oxidation; and γ is the stoichiometry coefficient of O$_2$ (C$_6$H$_5$CH$_3$ + 9O$_2$ → 7CO$_2$ + 4H$_2$O) which is equal to 9 [10,11].
In this equation, both kinetics constants follow the Arrhenius law as follows:

$$k_{Tu} = A_{Tu}\, e^{-\frac{E_a^{Tu}}{RT}} \qquad (5)$$

$$k_{O2} = A_{O2}\, e^{-\frac{E_a^{O2}}{RT}} \qquad (6)$$

RESULTS AND DISCUSSION

Structure
Since the identification of the used catalysts in the present work has previously been reported [9], no discussion is presented here on the structural properties of these catalysts. Therefore, only the catalytic performance of the prepared catalysts will be discussed, and the main focus of the present work will be on examining the catalytic activity in toluene oxidation.

Catalytic Activity
First of all, it should be mentioned that only oxidation products such as CO, CO$_2$ and H$_2$O were detected in toluene oxidation reaction. Figure 1a shows toluene conversion curves of the products over unmodified and zirconium modified Pt/HMS catalysts between 200 and 500 °C. This figure indicates that the activity of the Pt/Zr-HMS catalysts is high (~100%) under our experimental conditions while Pt/HMS catalyst exhibits lower activity, keeping below 83% of conversion at the highest temperature studied. CO$_2$ and H$_2$O are the major products of the reaction. However, non-negligible quantity of CO (near 6%) was formed with various catalysts (Fig. 1b). The order of the activity observed is: Pt/Zr(5)-HMS > Pt/Zr(35)-HMS > Pt/Zr(20)-HMS > Pt/HMS > Pt/Zr(10)-HMS. In Figs. 1(a and b), clearly toluene conversion for all prepared catalysts increases with increasing temperature. Furthermore, over the whole temperature range, the catalysts show approximately the same trend of CO$_2$ selectivity (Fig. 1b). The results show that the CO$_2$ selectivity is very close to 100%, and the CO selectivity is around 6%. These results show very good performance of the prepared catalysts, and it can be clearly observed that the Pt catalyst supported on Zr(5)-HMS presents remarkably higher catalytic activity than those of other catalysts.

Since the feed of this reaction (toluene) is a hydrocarbon that is a precursor for the coke, deactivation of catalysts will take place by coke deposition. Accordingly, 60 h stability tests have been performed at 350 °C on all undoped and doped Zr-HMS and the amount of coke deposited over the catalysts was measured by TGA technique (Fig. 2) that these values are as follows: Pt/HMS (0.77%), Pt/Zr(5)-HMS (1.02%), Pt/Zr(10)-HMS (0.54%), Pt/Zr(20)-HMS (0.99%)
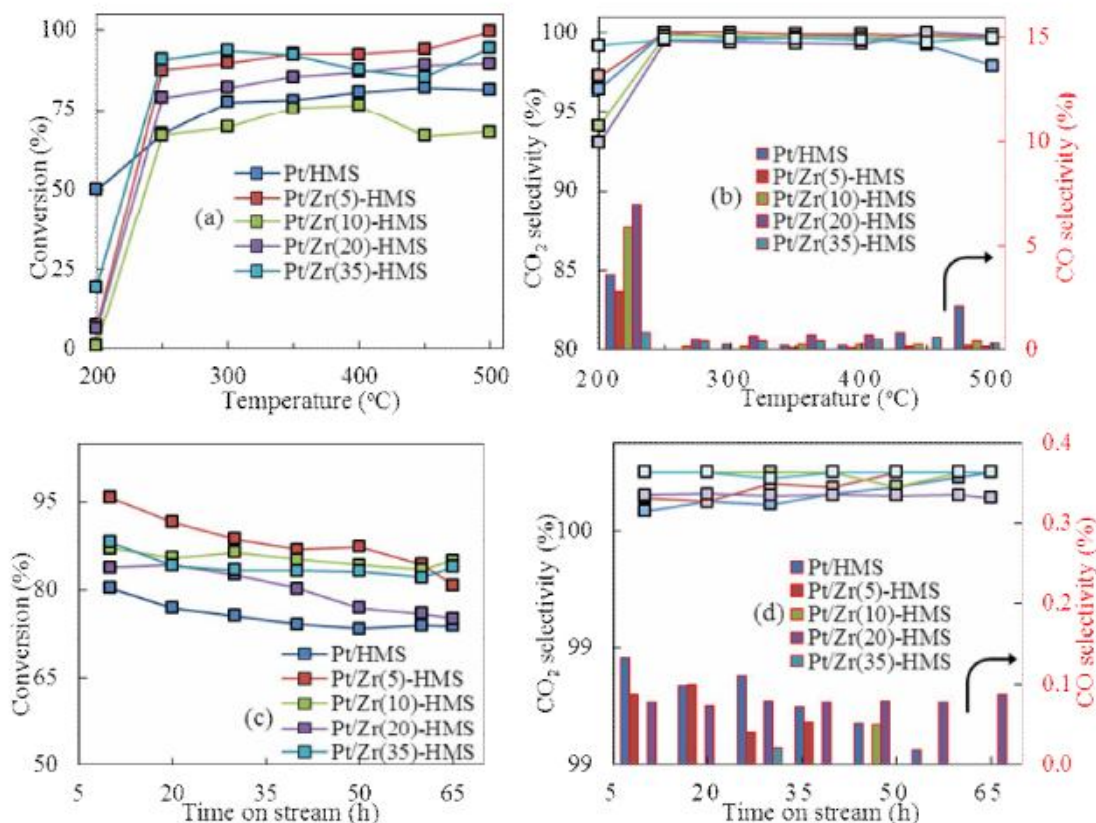
Fig. 1. Toluene conversion and catalytic selectivity to CO_2 and CO as a function of reaction temperature (a and b, respectively) and as a function of time on stream (c and d, respectively).

and Pt/Zr(35)-HMS (0.63%). The toluene conversion and selectivity to CO and CO_2 as a function of time are given in Figs. 1(c and d). As can be seen, the Pt/Zr(5)-HMS catalyst strongly is deactivated at the first hours. However, other catalysts smoothly linearly are deactivated over time. The process of decreasing the catalytic activity is in proportion to the coke values formed on the surface of these catalysts. In addition to acidity of catalysts as an effective factor in the formation of coke, it seems that dispersion of platinum on the surface of catalysts and their surface area are significant factors in the formation of coke.

Kinetics Study

The investigated results of the internal and external diffusion limitations show that there are no limitations by transport phenomena (diffusion regime) in the catalysts with

the smallest particles' size (50-150 μm) and the weights of catalysts below 0.5 g, and so, the catalytic activity under these conditions is generally affected by the kinetics regime. In order to recognize the fit kinetics model with the obtained experimental results, two kinetics models were evaluated and discussed independently.

The reaction kinetics were modeled by the empirical Power law (PL) at 200-500 °C temperature range based on the Eq. (1). For the experimental study, the initial flow rates of toluene and oxygen were varied from 1.5 to 3 ml h^{-1} and 12.6-50.4 ml min^{-1}, respectively.

Under these conditions, the range of toluene conversion was obtained 0.7% to 9.1%. It shows that the reaction proceeds in the kinetics regime. The observed reaction rates as a function of the partial pressures of the reactants in the logarithm form are shown in Fig. 3a. The results show that
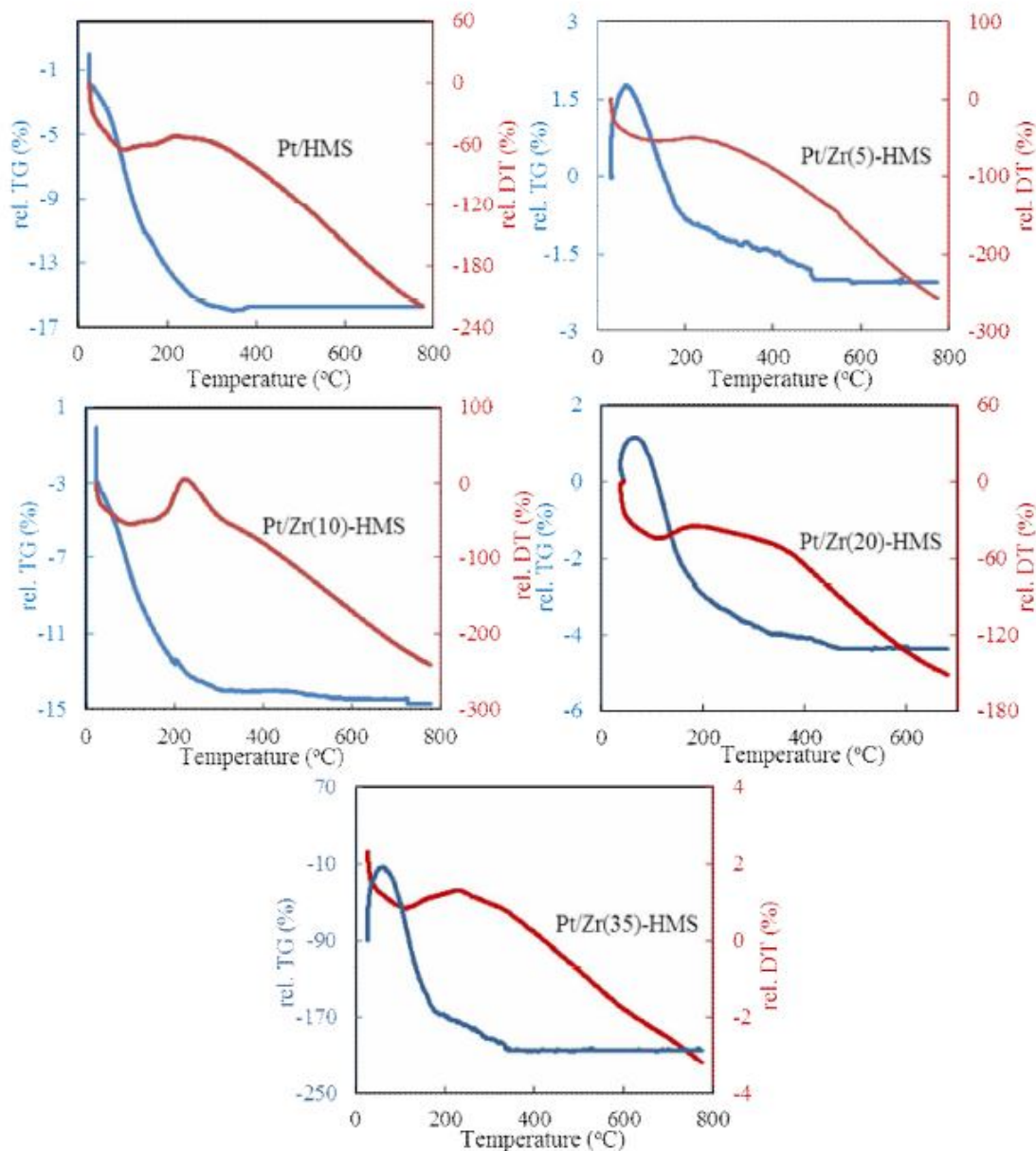
Fig. 2. TG-DTA curves of the spent catalysts after 60 h on stream.

the reaction rate increases with an increase in the pressure of toluene, whereas the reaction rate decreases slightly with an increase in the pressure of O$_2$.

By fitting the apparent rate constant results for the different catalysts to the Arrhenius equation (Eq. (2)) (Fig. 3b), the apparent activation energies set out in Table 1 have been estimated for the temperatures ranging from 200-500 °C. From the slope of these plots, the apparent activation energies were approximated to be in the range of 36.72-66.75 kJ mol^{-1}. These values show almost the observed conversion trend. It seems that the interaction of parameters as catalytic surface area, catalysts acidity and acid strength is effective on these results. The obtained data are very lower than the activation energies available
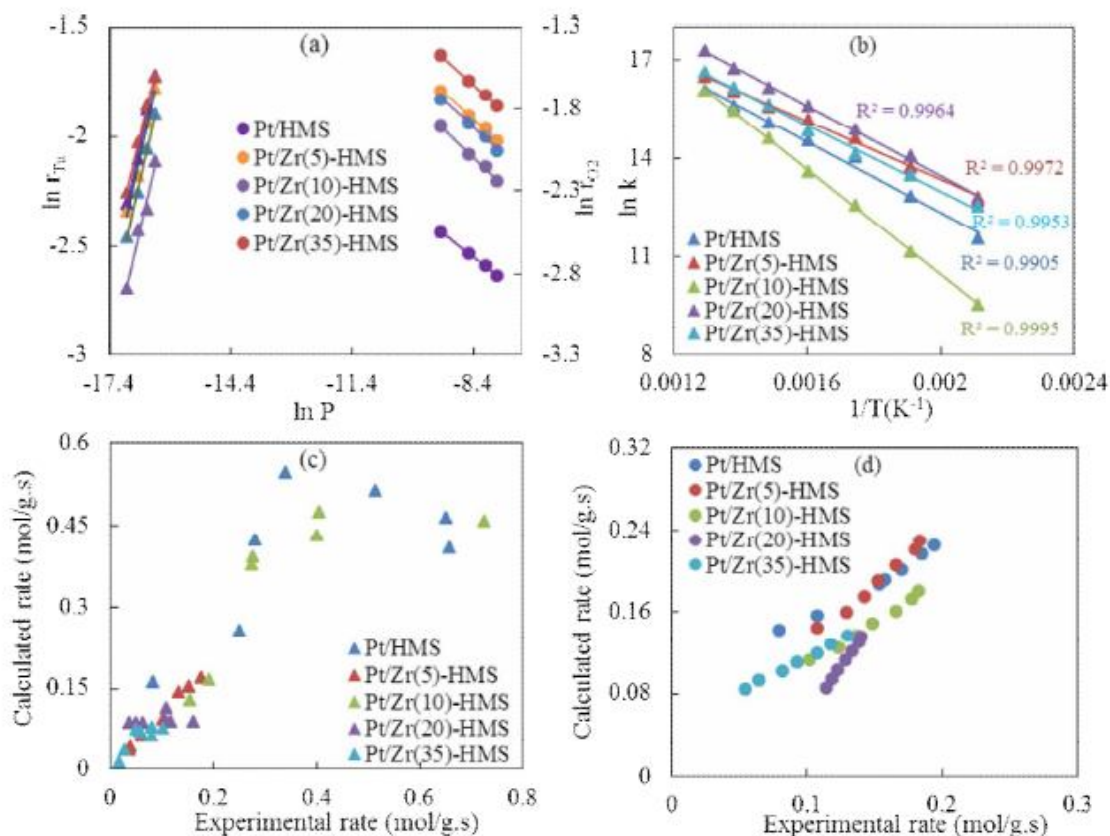
Fig. 3. (a) Double-log plots of the reaction rates *versus* the partial pressures of toluene and O_2 at a selected temperature (at 350 °C), (b) Arrhenius plots calculated from the experimental data, (c) estimated data by power law model, and (d) estimated data by Mars-van Krevelen model.

through the literature [12] for the gas-phase oxidation of toluene on supported catalysts. For example, Saqer *et al.* [13] reported activation energies of approximately 70-146 kJ mol^{-1} over binary mixtures of Cu, Mg and Ce oxides supported on γ-Al$_2$O$_3$ catalysts at 200-450 °C. Delimaris *et al.* [14] reported activation energies for the toluene oxidation over CuO-CeO$_2$ catalysts at temperatures between 160 and 260 °C to be 65-120 kJ mol^{-1}, whereas activation energies of 159.9 kJ mol^{-1} were reported by Behar *et al.* [11] in the toluene oxidation over nanosized Cu-Mn spinels at temperatures ranging from 77-427 °C.

Table 1 summarizes the parameters of the PR model (m and n) obtained by multiple regression analysis. The n and m values measured by this model show a slight negative reaction order for O_2 (-0.09– -0.25) and a value in the range of 0.98-1.23 for toluene as the reaction temperature raised

from 200 to 500 °C. The negative rate exponents of oxygen show the inhibitory effect of this compound and its strong adsorption on surfaces of catalysts in relation to the adsorption of toluene. The calculated reaction rates with this model were compared to the experimental rate values in Fig. 3c. The fitness of this model is evidenced by the correlation coefficient of data ($R^2 = 0.53$). These data indicate that the PR model is not consistent with the experimental results. The PR model is a simple statistical model versus numerical adjustment. Since this model does not consider the adsorption of molecules on catalytic surfaces, its result is unreal. Accordingly, to better estimate, other kinetics models (MVK model) were used in the study of toluene oxidation. The estimated values of the kinetics parameters in the MVK model (Eqs. (4-6)) and the fitting of this model to the experimental data are summarized and

Table 1. Kinetics Parameters at Various Temperatures over Platinated Catalysts for the VOCs Oxidation

	HMS		Zr(5)-HMS		Zr(10)-HMS		Zr(20)-HMS		Zr(35)-HMS	
	Power law model									
Temperature (°C)	n_{O2}	m_{Tu}	n_{O2}	m_{Tu}	n_{O2}	m_{Tu}	n_{O2}	m_{Tu}	n_{O2}	m_{Tu}
200	-0.25	0.99	-0.25	1.06	-0.25	0.81	-0.21	0.98	-0.23	0.88
250	-0.19	1.04	-0.18	1.09	-0.23	0.94	-0.15	1.07	-0.22	1.02
300	-0.18	1.06	-0.17	1.10	-0.21	1.01	-0.15	1.08	-0.19	1.04
350	-0.17	1.06	-0.16	1.11	-0.17	1.02	-0.14	1.14	-0.16	1.08
400	-0.17	1.08	-0.16	1.11	-0.14	1.06	-0.14	1.15	-0.14	1.13
450	-0.15	1.10	-0.15	1.13	-0.13	1.10	-0.14	1.16	-0.13	1.15
500	-0.09	1.15	-0.14	1.23	-0.11	1.13	-0.14	1.21	-0.12	1.17
E_{app}^{act} (kJ mol^{-1})	45.10		36.72		66.75		44.76		41.87	
	Mars-van Krevelen model									
A_{Tu} (s^{-1})	4.24×10^9		1.70×10^9		1.09×10^{12}		4.43×10^9		2.67×10^9	
E_a^{Tu} (kJ mol^{-1})	29.25		23.14		29.46		25.78		25.26	
A_{O2} (s^{-1})	6.38×10^{14}		8.73×10^8		2.23×10^{17}		9.00×10^{11}		6.24×10^{11}	
E_a^{O2} (kJ mol^{-1})	68.27		39.29		88.64		43.11		39.62	

presented in Table 1 and Fig. 3d, respectively. The correlation coefficient of this plot ($R^2 > 0.99$) is more than that for PR model. This shows that the calculated data for this model has a closely trend to experimental results and the deviation between the predicted and the experimental data is very little. So, MVK model can well predict the conversion behaviors of toluene oxidation.

CONCLUSIONS

According to the obtained results, Pt/Zr(5)-HMS is a suitable and stable catalyst for complete oxidation of toluene as a volatile organic compound. In the present work, the kinetics of this process was investigated in the air stream. The experimental results show that Pt/Zr(5)-HMS catalyst is more active than other prepared catalysts. The results obtained from two kinetics models show that the

Power law model is unsuitable for this reaction as the predicted data were against the experimental data, and the Mars-van Krevelen model can well predict the conversion behaviors of toluene oxidation.

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