Modified Micro/Mesoporous Catalysts for Deep Oxidation of Volatile Organics: Catalytic Performance and Kinetic Study

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   With the aim of eliminating toluene as a volatile organic compound, a collection of Pt-(Sn/Re)-HZSM-5/HMS catalysts with different weight percent of Sn/Re have been synthesized. Also, the catalytic performances of the prepared catalysts were compared to obtain the best activity and CO_2 and CO selectivity *versus* various catalyst weight percent, temperature (200-500 °C), and time on stream (1-65 h). The results show that incorporation of Sn and Re into Pt-HZSM-5/HMS structure promotes catalyst activity in which the high amount of 99.8% conversion obtained with PRSZH at T = 500 °C. Increasing temperature has an adverse effect on CO selectivity in all catalysts. The best CO_2 selectivity (100%) was observed at 500 °C and Pt(0.3 wt%)-Sn(0.3 wt%))-HZSM-5/HMS. The proper kinetics study leads to suitable decisions about catalytic performance. Employing two models, it was possible to provide good information about the kinetic behavior of the prepared catalysts. Although both modeling methods exhibit outstanding performances, however, kinetics data reveal that Mars-van Krevelen model has better performances compared to the Power law model.

Keywords: Toluene oxidation, Kinetics, Power law model, Mars-van Krevelen model, Selectivity

INTRODUCTION

   Nowadays, VOCs are one of the common causes of environmental pollution due to a large variety of sources, including fossil fuel combustion, motor vehicle, and coal-fired power plants. The catalytic oxidation method remains a promising and sustainable technique to remove VOCs and produce green products (a mixture of CO_2 and H_2O) [1].

   One of the essential interests in this reaction is to find highly active and selective catalysts [2]. Noble metals supported catalysts have demonstrated higher activity and durability in VOCs catalytic oxidation [3]. To be economical, the synthesized catalysts are usually modified by some metals such as bi- and tri-metal that can produce properties similar to noble metals.

   These bi- and tri-metallic phases are effective in increasing the eventual cooperative properties. These properties improve the selectivity to deep oxidation by increasing oxygen mobility. They also increase the catalytic activity by stabilizing more active metal species and improve redox cycles for the reactivation of the catalyst.[2] Numerous studies present the successful performance of Mn, Co, Al, and Cu in the oxidation of VOCs [4-9]. But in the present work, we have used a different metal mixture (Pt-Re-Sn) which has shown good results in other catalytic processes. The various reported works have shown that these metals interact with Pt by chemical affinity, and so modify the catalytic activity, selectivity, and stability [10-12].

   In the present work, the performance of this metal mixture on micro/mesoporous catalysts was investigated in the oxidation reaction of a model volatile organic compound. Many various model compounds (benzene, toluene, ethanol,

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butanol, formaldehyde, *etc.*) were used for the investigation of the VOCs behavior [1,2,13,14]. As you know, toluene is one of these compounds that industrial, petrochemical, and many other human activities are the source of production of this substance in the environment. Since this substance is highly volatile and its destructive effects on human health and the environment [15], the oxidation of this substance as a model of volatile organic compounds is the subject of many research studies (as this work).

Herein, we exploit the oxidation activities of Pt-HZSM-5/HMS in the elimination of toluene. Sn and Re are coupled discretely and jointly with this mico/mesoporous catalyst for modifying the product selectivity.

EXPERIMENTAL

Catalyst Preparation and Characterization Methods

A series of bi- and tri-metallic Pt-HZSM-5/HMS catalysts with 30 wt% and different weights percent of Re and Sn were prepared using the impregnation method. These weights percent varied from 0 to 0.3 wt%. Novel Pt-HZSM-5/HMS catalysts with different Re and Sn weights percent were named as PRZH, PSZH, PRSZH, and PSRZH, respectively, instead of Pt(0.3 wt%)-Re(0.3 wt%)-HZSM-5/HMS, Pt(0.3 wt%)-Sn(0.3 wt%))-HZSM-5/HMS, Pt(0.3 wt%)-Re(0.2 wt%)-Sn(0.1 wt%)-HZSM-5/HMS and Pt(0.3wt%)-Sn(0.2 wt%)-Re(0.1 wt%)-HZSM-5/HMS. In this method, an aqueous solution was prepared using the required amounts of ammonium perrhenate and tin(II) chloride. Pt-supported catalysts were prepared by impregnating appropriate solutions of hexachloroplatinic acid. In a nutshell, the Pt-(Re/Sn)-HZSM5/HMS support was made up by increasing the HZSM-5 zeolite to the initial solution of the HMS colloidal precursor and then impregnation method with Pt, rhenium, and tin. The following materials were used for this synthesis: ethanol, tetraethyl ortho silicate (TEOS) as a silica source, dodecylamine (DDA), hydrochloric acid (1 M), distilled water, hexachloroplatinic acid, tin chloride (SnCl$_2$.2H$_2$O) and ammonium per-Renate (NH$_4$ReO$_4$), as a source of platinum, rhenium, and tin, respectively.

The temperature conditions used for synthesis are as follows: 110 °C overnight for crystallized catalyst to dry;

600 °C in the air for 6 h for calcination; 300 °C for 4 h in the air for solvent evaporation and drying after platination. The details of the preparation, plus all the characterization tests, including XRD, XRF, NH$_3$-TPD, H$_2$-TPR, FTIR, H$_2$ chemisorption, nitrogen sorption, and TGA procedures are given elsewhere [11].

Catalytic Tests

A quartz fixed bed reactor at atmospheric pressure was used with the air flow rate of 3 ml s^{-1}, 0.3 g of the catalyst, toluene flow rate of 2 ml h^{-1}, and temperature range of 200 to 500 °C. Before the oxidation, each catalyst was pretreated at 400 °C for 2 h under the He stream. 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) are the components of a system to study this catalytic oxidation. H$_2$O, CO, and CO$_2$ are the only products of this reaction and no other product was observed in our reaction conditions. Stability test was also performed with the same reactant mixture as mentioned above, at 350 °C for 60 h.

Kinetic Tests

For investigating the kinetic reaction, the reactants (mixture of toluene and O$_2$) in the vapor-phase were tested over prepared catalysts. Consequently, the order of toluene and oxygen was estimated by changing the partial pressure dependency on oxygen as well as changing the partial pressure dependency on toluene, in the gas phase at a constant temperature in the range of 200-500 °C and ambient pressure.

The reaction rate was defined as follow:

$$rate \ (mol \ g^{-1} \ s^{-1}) = \frac{Tu \text{ flow rate} \times Tu \text{ density} \times \text{conversion (\%)}}{Tu \text{ molar weight} \times \text{weight of catalyst} \times \text{impregnated metal}} \quad (1)$$

RESULTS AND DISCUSSIONS

Pt-(Re-Sn)-HZSM-5/HMS Catalysts Characterization

Since the characterization of the prepared catalysts has been reported in our previous work [10] the structural properties of these catalysts are not discussed here. The

purpose of this study is only to investigate the activity of catalysts that have already been identified [10].

Catalytic Activity

To investigate the effect of Re and Sn on the catalytic activities of toluene deep oxidation over Pt-HZSM-5/HMS catalyst, catalytic evaluation experiments were carried out at 200-500 °C.

As mentioned before, CO, CO_2, and H_2O are the only detected oxidation products. The catalytic results with regard to the conversion of toluene and selectivity to CO_2 and CO are presented in Figs. 1 to 4.

It is obvious from Fig. 1 that the catalysts modified with higher amount of Sn present greater and near activity to PZH catalyst than other prepared catalysts.

However, this greater activity moves to higher temperatures for the conversion of toluene as well as for the production of CO_2.

This result can be explained based on a summary of the results obtained from the characterization of the prepared catalysts[10] as below:

S_{BET} (m^2 g^{-1}): PZH > PSZH > PSRZH > PRSZH > PRZH

V_p (cm^3 g^{-1}): PZH > PSRZH > PRSZH > PSZH > PRZH

d_p (nm): PZH > PSRZH > PRSZH > PSZH > PRZH

weak acid: PZH > PRZH ~ PSRZH > PRSZH ~ PSZH

strong acid: PZH > PRZH > PRSZH > PSRZH > PSZH

Pt_d: PZH > PSZH > PRSZH > PSRZH > PRZH

Si/Al: PSZH > PSRZH > PRSZH > PRZH > PZH

These results show that the surface area (S_{BET}), dispersion of platinum (Pt_d), and Si/Al are the factors affecting the activity of PSZH catalyst and increasing the acidity has an adverse effect on its activity.

For ease of comparison, the performance of the catalysts in selectivity to CO_2 and CO were shown in Fig. 2. In accord with this figure, the PSZH catalyst has the closest selectivity to the PZH catalyst.

Since the reactant in the present work (toluene) is a hydrocarbon, the formation of coke on the surface of the catalysts is inevitable.

Based on this, the amount of coke on the surfaces of the catalysts was investigated. To examine the stability of the catalysts and coke deposition over the catalyst surfaces, the experiments went on a continuous stream for 65 h at an optimum temperature (350 °C).
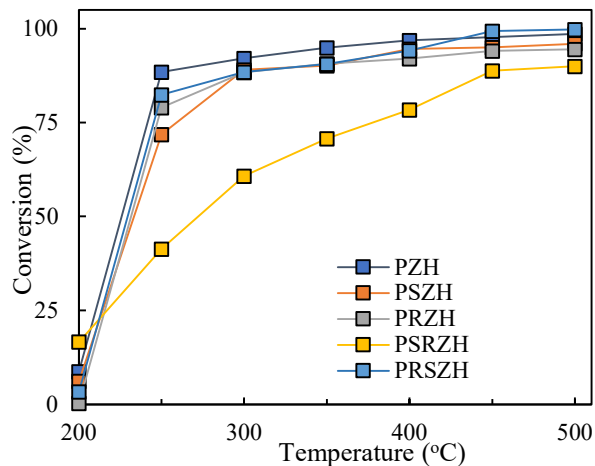

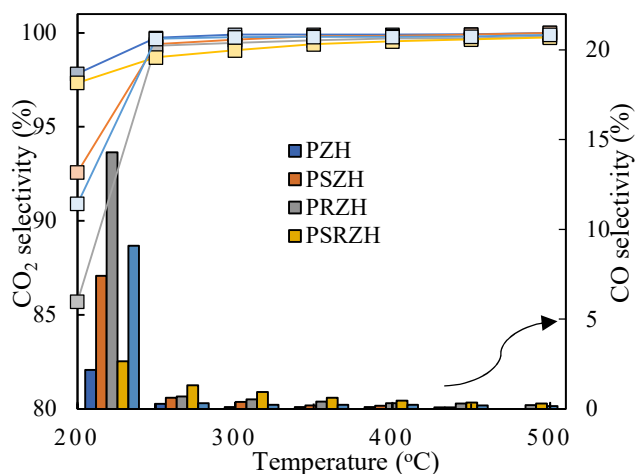**Fig. 1.** Toluene conversion as a function of reaction temperature.

Fig. 2. Selectivity to CO_2 and CO in toluene oxidation *versus* reaction temperature.
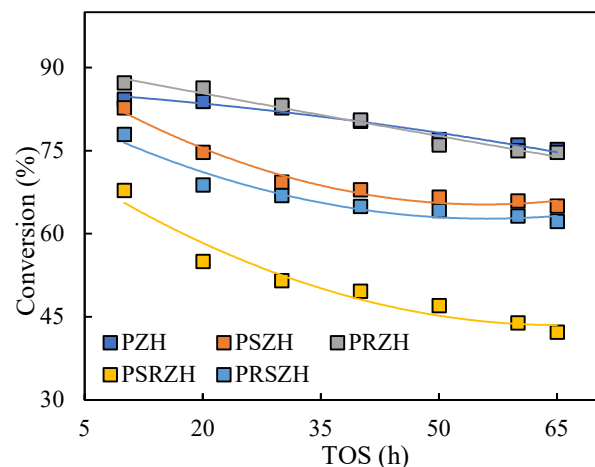

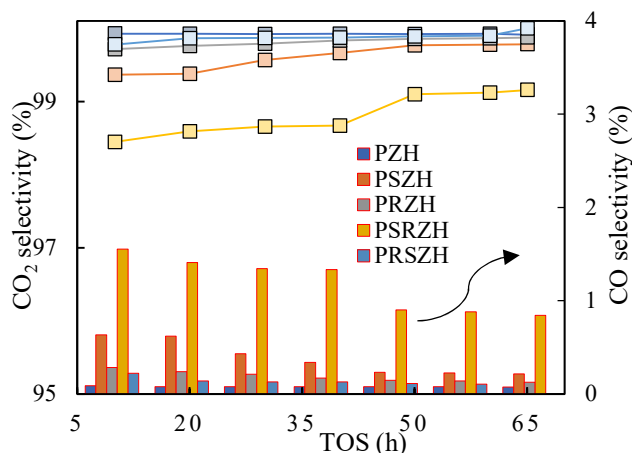**Fig. 3.** Toluene conversion as a function of time on stream (TOS).

Fig. 4. Selectivity to CO_2 and CO in toluene oxidation *versus* time on stream (TOS).

Total conversion and selectivity to CO and CO_2 after 65 h on stream over the prepared catalysts are presented in Figs. 3 and 4. All catalysts experience a decrease in conversion over time due to the catalyst being deactivated following the deposition of coke on the active sites of the catalysts. The highest total conversion was found over PRZH. This catalyst has the closest change in conversion to the PZH catalyst at this time on stream. Other catalysts show a sharp drop in toluene conversion. This phenomenon is related to the different textural properties of the studied catalysts.

The results of selectivity (Fig. 4) show all catalysts except PSRZH show high selectivity to CO_2. However, the lowest selectivity for CO after PZH catalyst is for PRSZH catalyst and the highest CO selectivity is for PSRZH catalyst, which is very undesirable.

Kinetic Study

The empirical power rate model (PRM) was used for modelling and measuring the order of each reactant based on the following equation:

$$rate\ (mol\ g^{-1}\ s^{-1}\ ) = k P_{O2}^n P_{Tu}^m \qquad (1)$$

Where k is the rate constant, P_{O2} and P_{Tu} are the partial pressures of oxygen and toluene, and n and m are the orders of the reaction with respect to the oxygen and toluene partial

pressures, respectively.

To derive kinetic parameters of the toluene oxidation reaction on the prepared catalysts, 0.3 g samples were used and the catalytic activities were tested separately at toluene flow rates in the range of 1.5 to 3 ml h^{-1}, O_2 flow rates of 60-240 ml min^{-1}, and reaction temperatures of 200-500 °C as well.

According to these conditions, the logarithmic form of reaction rates against the reactant (oxygen or toluene) pressure was generally linear. The slopes of these lines express the order of reaction for each component.

To measure the apparent activation energy (E_{app}^{act}), the Arrhenius equation (Eq. (2)) was used for this reaction over each catalyst. Also, the logarithmic form of this equation versus reverse temperature was applied for evaluating the rate constant (k).

$$k = A\ e^{-\frac{E_{app}^{act}}{RT}} \qquad (2)$$

It should be noted that in order to control the reaction only under the influence of the kinetic regime, the conversion was kept less than 10% [16].

The logarithm forms of the reaction rates at 300 °C *versus* the partial pressures of the reactants were shown in Fig. 5a. The results show that the reaction rate behavior is different with increasing oxygen and toluene pressures. The rate decreases with increasing oxygen pressure and increases with increasing toluene pressure. According to PR model, the slope of these plots shows the partial orders to oxygen and toluene, which are summarized in Table 1.

The negative partial reaction order for O_2 (0.00 – -0.40) and the positive values in the range of 0.85-1.17 for toluene were observed. The negative rate exponents show the inhibitory effect on the reaction and the positive values present the strong adsorption of the component over the catalysts surfaces.

To show the performance of this mathematical model, Figure 5 b shows the reaction rate values calculated by this model against the experimental values. The fitness of this model is demonstrated by the correlation coefficient of data that is R^2 =1.0 for all catalysts except PRSZH catalyst. Despite the good results that have been obtained by the PR model, since it is a simple mathematical model and does not
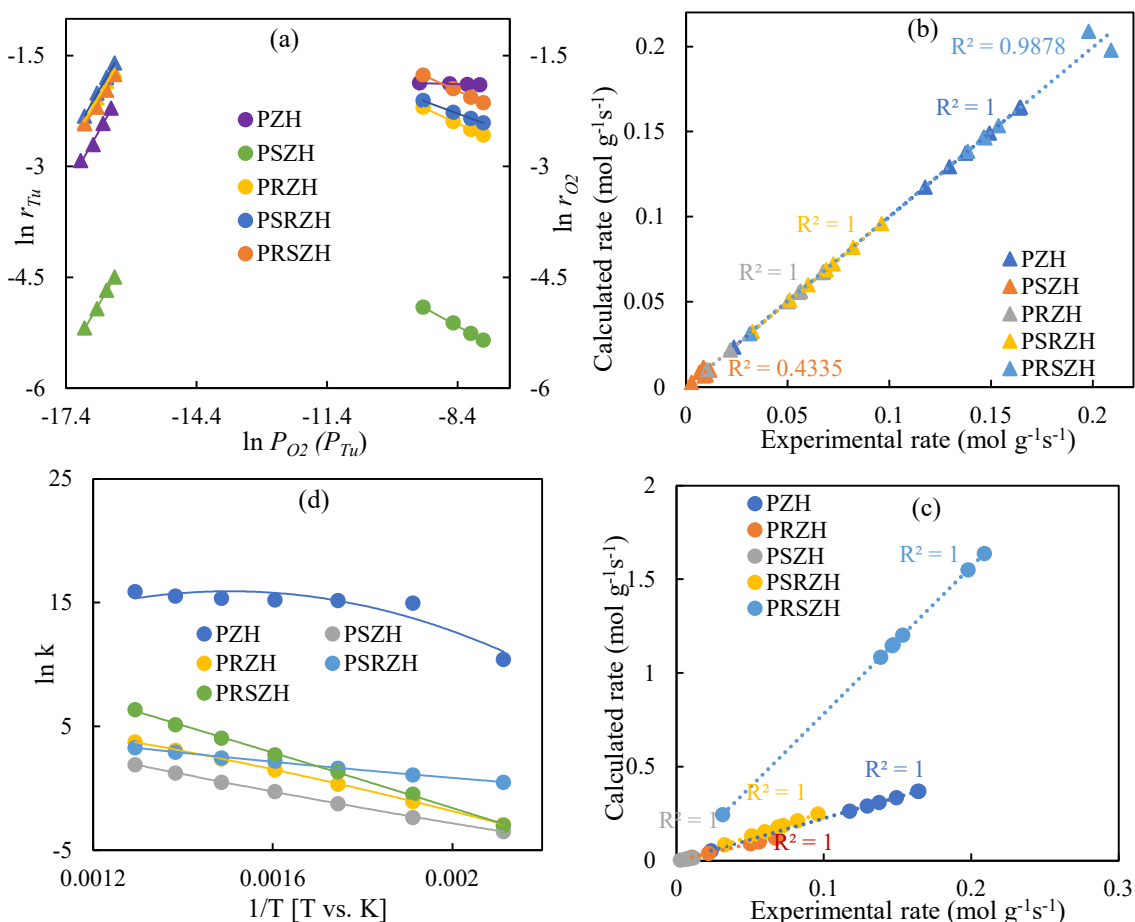
Fig. 5. (a) double-log plots of the reaction rates *versus* the partial pressures of toluene and O₂, (b) estimated data by power law model, (c) estimated data by Mars-van Krevelen model, and (d) Arrhenius plots calculated from the experimental data.

consider surface adsorptions, another model was used to study catalytic interactions.

Consequently, to better estimate and obtain real results, another kinetic model, Mars-van Krevelen (MVK) model was used in the kinetic study of toluene oxidation. This model has a two-step mechanism that involves the reaction of adsorbed toluene with the oxygen on the catalyst and re-oxidized of the reduced metal oxide by oxygen [16]. The rate of toluene oxidation can be expressed by the following equation:

$$rate = \frac{k_{O2}k_{Tu}P_{O2}P_{Tu}}{\gamma k_{Tu}P_{Tu}+k_{O2}P_{O2}} \quad (3)$$

where, $rate$: 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; γ is the stoichiometry coefficient of O₂ ($C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$) which is equal to 9.[16] In this equation, both kinetic constants are as follows:

$$k_{Tu} = A_{Tu}\ e^{-\frac{E_a^{Tu}}{RT}} \quad (4)$$

$$k_{O2} = A_{O2}\ e^{-\frac{E_a^{O2}}{RT}} \quad (5)$$

The estimated values of the kinetic parameters in this model were summarized in Table 1. The fitting of this model to the experimental data (Fig. 5c) presents a good correlation

Table 1. Kinetics Parameters and Activation Energies were Obtained from Power Law and Mars-van Krevelen Models

T (°C)	Orders	PZH	PSZH	PSRZH	PRSZH	PRZH
			Power law model			
200	n_{O2}	-0.16	-0.38	-0.30	-0.39	-0.40
250	n_{O2}	-0.03	-0.32	-0.25	-0.36	-0.33
300	n_{O2}	-0.02	-0.32	-0.22	-0.27	-0.27
350	n_{O2}	-0.02	-0.24	-0.20	-0.26	-0.21
400	n_{O2}	-0.02	-0.24	-0.20	-0.20	-0.20
450	n_{O2}	-0.01	-0.22	-0.18	-0.08	-0.19
500	n_{O2}	0.00	-0.14	-0.17	-0.05	-0.13
200	m_{Tu}	0.93	1.00	0.99	0.85	0.97
250	m_{Tu}	1.03	1.00	1.00	0.93	1.02
300	m_{Tu}	1.04	1.00	1.03	0.96	1.02
350	m_{Tu}	1.04	1.05	1.04	0.96	1.04
400	m_{Tu}	1.05	1.09	1.05	1.01	1.07
450	m_{Tu}	1.06	1.15	1.06	1.08	1.08
500	m_{Tu}	1.07	1.17	1.07	1.09	1.09
	E_{app}^{act} (kJ mol^{-1})	42.40	55.06	28.08	92.40	67.26
			Mars-van Krevelen model			
K	E_{app}^{act} (kJ mol^{-1})	31.98	31.98	18.04	71.73	52.00
	A (mol g^{-1}s^{-1})	2.55×10^{-22}	2.55×10^{-22}	2.26×10^{-18}	3.11×10^{-26}	1.26×10^{-23}
K_{Tu}	$-\Delta H_{ads-Tu}$(kJ mol^{-1})	4.97	4.97	4.97	4.66	4.97
	A_{Tu} (atm^{-1})	4.99×10^{-9}	64.88	64.88	70.30	64.88
K_{O2}	$-\Delta H_{ads-O2}$(kJ mol^{-1})	4.38	20.31	29.48	59.18	46.31
	A_{O2}(atm^{-1})	1.26×10^{-2}	6.93×10^{11}	1.26×10^{10}	7.07×10^{7}	7.00×10^{8}

coefficient for these plots ($R^2 = 1.0$). This shows that the calculated data from this model has a close trend to experimental results. So MVK model can well predict the conversion behaviors of toluene oxidation.

Figure 5d presents the Arrhenius plots. By fitting the experimental data to Eq. (2), the slopes of these plots for the temperatures ranging from 200 to 500 °C are the apparent activation energies summarized in Table 1. Since the reaction rate and activation energy are inversely related, according to the obtained data of activation energies, the PSRZH catalyst has the highest reaction rate.

CONCLUSIONS

The aim of the present study was to investigate the bi-

and tri-metallic catalysts for toluene oxidation to boost the quality of exhaust gases from pollutants. In this way, the collections of the Pt-(Sn/Re)-HZSM-5/HMS catalysts with various Sn/Re weights percent were prepared. The effect of Sn and Re amounts on the activity and CO and CO_2 selectivity in the temperature range of 200-500 °C and time on stream of 1-65 h were analyzed. The kinetic study was employed to find the best-prepared catalysts versus influencing preparation parameters of catalyst such as weight percent and temperature. Also, two techniques for modelling the kinetics of this reaction were compared together. Based on the obtained results, the following conclusions can be drawn:

1) The incorporation of Sn and Re in the Pt-ZHZSM-5/HMS structure promotes catalyst activity. The amount of

conversion was increased with increasing temperature in all catalysts and maximum conversion of 99.8% happens at PRSZH and T = 500 °C.

2) Unlike CO selectivity, selectivity to CO_2 increased with increasing temperature in all catalysts. The maximum value of CO_2 selectivity (100%) and minimum amount of CO selectivity (0%) were observed at 500 °C and PSZH.

3) CO_2 selectivity elevates with an increasing time on stream considerably. The stability results show that catalyst deactivation over time through the coke deposition is very low. Also, the PRZH catalyst has the same results as PZH.

These results show that a collection of parameters such as catalytic surface area, catalyst acidity, and acid strength effect on these results. Moreover, the remarkable kinetic performances disclose that the PSRZH catalyst can effectively and quickly advance the reaction. According to modelling results, the Mars-van Krevelen model has more significant and slightly better results compared to the Power law model.

ACKNOWLEDGEMENTS

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