

Application of SnO₂/Alumina Nanocatalyst in Removal of Naphthenic Acids from Crude Oil

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Highlights

- SnO₂/Al₂O₃ was synthesized as a mesoporous nanocatalyst.
- SnO₂/Al₂O₃ nanocatalyst was used to convert naphthenic acids of crude oil.
- The naphthenic acids were removed by catalytic esterification with methanol to reduce their harmful effects.
- The optimal conditions for the catalytic esterification of naphthenic oils process were determined, and, under these conditions, 83% of the naphthenic acids were removed.

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Abstract

The separation of naphthenic acids from crude oil is difficult, and the presence of such materials in crude oil reduces its value. In this work, using catalytic esterification with methanol, naphthenic acids of crude oil were removed to reduce their harmful effects. SnO₂/γ-Al₂O₃ nanocatalyst was synthesized and used to convert naphthenic acids of crude oil in a fixed bed catalytic reactor. The nanocatalyst was characterized by the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and Brunauer–Emmett–Teller (BET) surface area techniques. The XRD revealed the formation of rutile SnO₂ on alumina, and the FESEM approved that the catalyst is comprised of nanoparticles with a diameter in the range of 50 to 90 nm. The BET indicated that the catalyst has a mesopore structure with a surface area of 213.4 m²·g⁻¹. The optimal conditions for the catalytic esterification process of naphthenic oil were determined. The temperature of the reduction of the total acid number (TAN) of crude oil ranged from 250 to 360 °C, and the TAN was reduced to less than 0.5 mg KOH/g in this temperature range. A methanol-to-oil ratio (M/O) of 2 wt %, a velocity space of 2.5 h⁻¹, a reaction temperature of 300 °C, and atmospheric pressure were selected as the optimal conditions for the removal of naphthenic acids. Under these conditions, 83% of naphthenic acids was removed. The study indicated that SnO₂/γ-Al₂O₃ could be a promising nanocatalyst for the reduction of total acid of crude oil under mild conditions.

Keywords: Crude Oil, Nano Tin Oxide, Naphthenic Acids, Space Velocity, Total Acid Number

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1. Introduction

Crude oils from many parts of the world, including China, India, Venezuela, Eastern Europe, Russia, and the USA are often reported to be naphthenic oils. Such oils have been found to contain organic acids with saturated ring structures and one or more carboxylic groups (Cox, 2013). While the acids varied considerably in molecular weight, their general formula, like that of all naphthenic acids, could be written as $R[CH_2]_nCOOH$, where R is usually a cyclopentane or cyclohexane ring (Derungs 1956; Slavcheva, Shone et al., 1999). The most well-known organic acids in crude oil and petroleum products (motor oil) are naphthenic acids and aliphatic acids.

Naphthenic acids (NAs), which is a mixture of alicyclic carboxylic acid and saturated aliphatic acid, are a component of heavy crude oil and responsible for the acidity of heavy crude oil (Mandal and Sasaki, 2018).

The total acid number (TAN) of crude oil can range from 0.01 to 16.2 mg KOH/g depending on the reservoir rock and the crude oil production area. A crude oil with a total acid number in the range of 0.6 to 0.1 mg KOH/g is often used as a corrosion mitigation tool (Anderson et al., 2013). Thermal decomposition as a noncatalytic destructive method is ineffective in the reduction of the acidity of heavy crude oil at a high temperature. High temperatures almost offer thermal cracking of heavy crude oil and result in coke formation (Mandal and Sasaki, 2018). The presence of NAs in heavy crude oil poses a great challenge to the exploration of the crude oil because they have corrosive properties. The removal of naphthenic acid compounds from crude oil is known as the most important process in upgrading heavy oil. There are different ways to reduce the TAN of crude oil. Caustic washing and blending heavy acidic crude oil with conventional crude oil are two conventional methods used in the removal of NAs from heavy crude oil. The disadvantage of blending method is its low removal efficiency (2–3%) (Khan et al., 2017), and the NAs are not often removed completely from the blend. In addition to the above methods, other approaches such as treatment with ionic liquids (Martinez-Palou and Luque, 2014), catalytic esterification (Li et al., 2013; Duncum and Osborne, 2002; Blum et al., 1998), catalytic decarboxylation (Zhang et al., 2006; Fu et al., 2008), treatment with ammonia solution (Wang et al., 2006), microwave irradiation (Huang et al., 2006), physical adsorption (Silva et al., 2013), and solvent extraction (Shah et al., 2016) have been proposed to reduce the TAN of crude oil. Nevertheless, these processes have certain drawbacks that should be addressed carefully prior to practical implementation. For example, although the TAN can be reduced by catalytic processes, ionic liquids, or ammonia route, the use of expensive chemicals, heterogeneous catalysts, and hydrogen makes these methods economically unfavorable. Catalytic routes have been explored for the direct reduction of the TAN of high-acid crudes (HACs) using alkali and alkaline earth metal oxides (Li et al., 2013; Redondo et al., 2020) and hydrotalcite (Li et al., 2013; Redondo et al., 2020). The esterification of NAs with alcohols utilizing metal carboxylates and oxides as the catalyst is a promising approach to removing NAs, especially from high acidity crude oil. However, esterification using these catalysts usually requires a high reaction temperature and a relatively long reaction time, making it necessary to develop other catalysts and other techniques. There are few works on the esterification of the naphthenic acids of acidic crude oil using solid catalysts. Some works have reported using zeolites such as Amberlite15 and heteropoly acids (HPAs) supported on silica (HPA/silica) as the catalyst (Altiokka and Çıtak, 2003; Das and Parida, 2007). They reported that the reaction is relatively slow, so, to obtain a reasonable conversion, it is required to employ either higher temperatures or a higher amount of catalyst. The application of 12-tungstophosphoric acid (TPA) supported on $\gamma\text{-Al}_2\text{O}_3$ catalyst for the removal of the naphthenic acids from crude oil was also reported by Rana et al. (2018).

In this paper, for the first time, nano tin oxide supported on $\gamma\text{-Al}_2\text{O}_3$ with a high surface area was synthesized and used as a nanocatalyst for the catalytic removal of naphthenic acids from Iran's crude

oil. Different factors affecting the removal of NAs from crude oil in the process of catalytic esterification over SnO₂/γ-Al₂O₃ were investigated, and the catalyst was characterized by the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and Brunauer–Emmett–Teller (BET) surface area techniques.

2. Experimental procedures

2.1. Materials and measurements

All the chemicals and solvents were reagent or analytical grade and used as received. They were supplied from Merck Company. The crude oil was obtained from Tabriz refinery of Iran.

2.2. Catalyst preparation

Sodium hydroxide (2 g) was diluted with distilled water to a volume of 20 mL, and 5 g of SnCl₂ and 20 mL of ethylene glycol were added to the solution drop by drop while it was mixing for 2 h. The formed precipitate was filtered by centrifuging, then washed twice by distilled water, and finally dried at a temperature of 100 °C for 4 h. Annealing treatment was performed at 250 °C for 3 h to obtain the final SnO₂ powder. To prepare SnO₂/γ-Al₂O₃ catalyst, SnO₂ and γ-Al₂O₃ at a mass ratio of 1:1 was mixed in 50 mL of ethanol for 2 h; then, it was filtered and dried at 70 °C. Finally, it was treated at 250 °C for 3 h.

2.3. Catalyst characterization

The XRD analysis was used for the phase characterization of the catalyst by using Siemens 5000 and a copper lamp with a wavelength of 0.154 nm. The FESEM analysis was employed to examine the size and the morphology of the catalyst nanoparticles using Zeiss scanning spectroscopy. The BET specific surface areas, the pore diameter, and the pore volume of the catalyst were measured by using N₂ adsorption–desorption at 77 K using the Micromeritics ASAP 2020 instrument.

2.4. Catalytic process of NAs removal

Crude oil (100 g) and methanol (1–3 wt % of crude oil) were mixed together and stored in a tank reactor equipped with a mechanical mixer and heater. During the test, the resulting mixture was stirred constantly to form a uniform solution. SnO₂/γ-Al₂O₃ catalyst (1 g) was added into the mixture, and the reaction was performed under reflux conditions at different temperatures (180–360 °C) for 2.5 h. Using a decanter, the produced water was removed from the oily product. Then, the oily product was treated with anhydrous sodium sulfate as a water adsorbent. The oily product was distilled before being analyzed by the gas chromatograph. A schematic of the setup is shown in Figure 1. The equation for the catalytic esterification reaction of petroleum acids with alcohols, which produces esters and water, is expressed in Scheme 1.

3. Results and discussion

3.1. Catalyst characterization

According to the XRD pattern of the SnO₂/γ-Al₂O₃ catalyst shown in Figure 2, only the reflex bands of SnO₂ are detectable; however, they are slightly shifted to smaller *d* values. The XRD pattern of the catalyst is comparable with the standard (Card no: 88-0287), indicating the formation of the rutile phase since the reflex bands assigned to the crystalline γ-Al₂O₃ are much weaker compared to those corresponding to SnO₂, and the related bands are not observable.

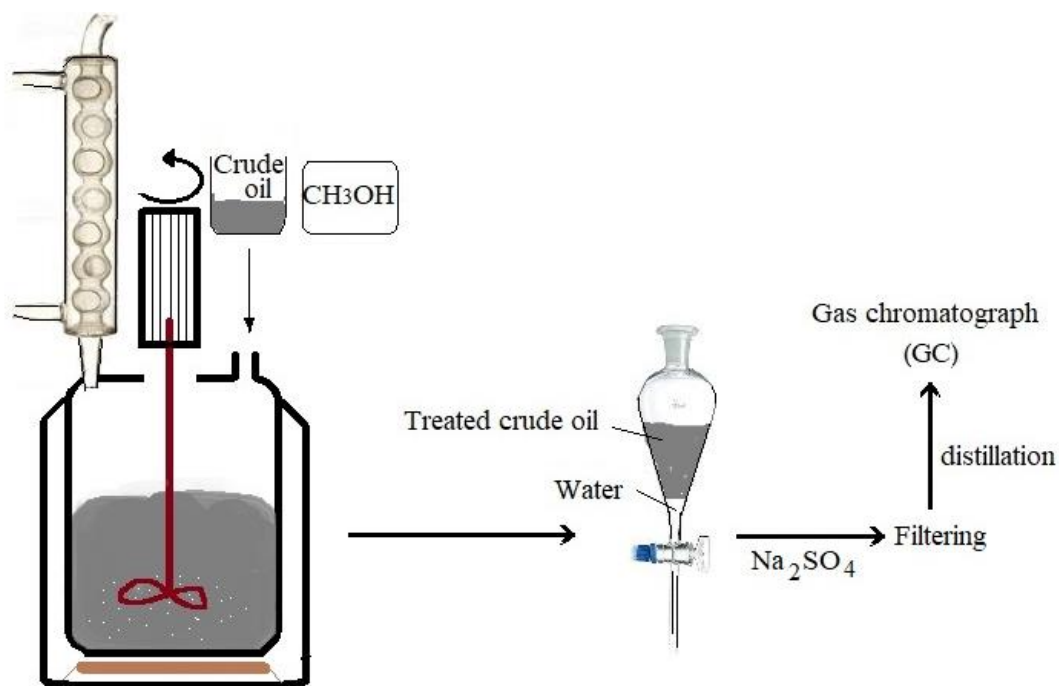
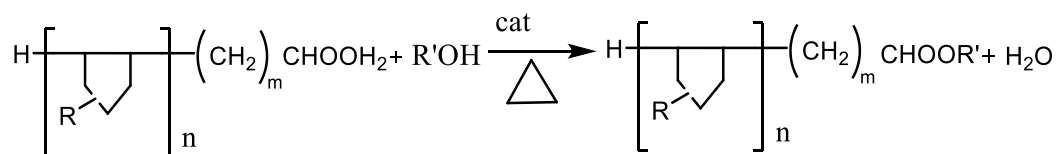


Figure 1

A schematic of the experimental setup.



Scheme 1

The reaction of naphthenic acids of crude oil with methanol at high temperatures.

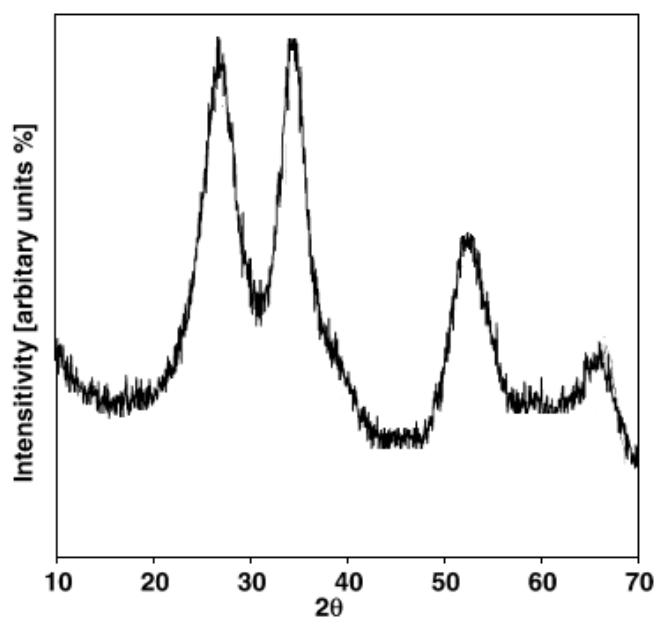


Figure 2

The XRD pattern of the $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst.

Figure 3 depicts the FESEM images of the SnO₂/ γ -Al₂O₃ catalyst. The particle size of the catalyst is smaller than 100 nm, typically in the range of 50–90 nm. It can be seen that the nanoparticles are absorbed due to the presence of electrostatic forces and created a clumpy state.

Since the pure SnO₂ has a low surface area, and one of the characteristics of a catalyst is its high surface area, the SnO₂ was supported on gamma alumina due to its high surface area. The adsorption isotherms of the SnO₂/ γ -Al₂O₃ catalyst follow type V and the hysteresis type H1 in the IUPAC classification, which indicates that the SnO₂/ γ -Al₂O₃ catalyst is mesoporous and consists of well-defined cylindrical-like pore channels or agglomerates of approximately uniform spheres.

Table 1 presents the surface area, the Barrett–Joyner–Halenda (BJH) average pore size, and the BJH adsorption cumulative pore volume of the catalyst. According to Table 1, the surface area of the nanocatalyst is 213.4 m²·g⁻¹. The BJH average pore size distribution of the catalyst is also delineated in Figure 4, which indicates that the catalyst has a high surface area and a wide pore diameter distribution (3–45 nm), allowing the molecules of naphthenic acids of any length and diameter to enter the pores of the catalyst under the right conditions.

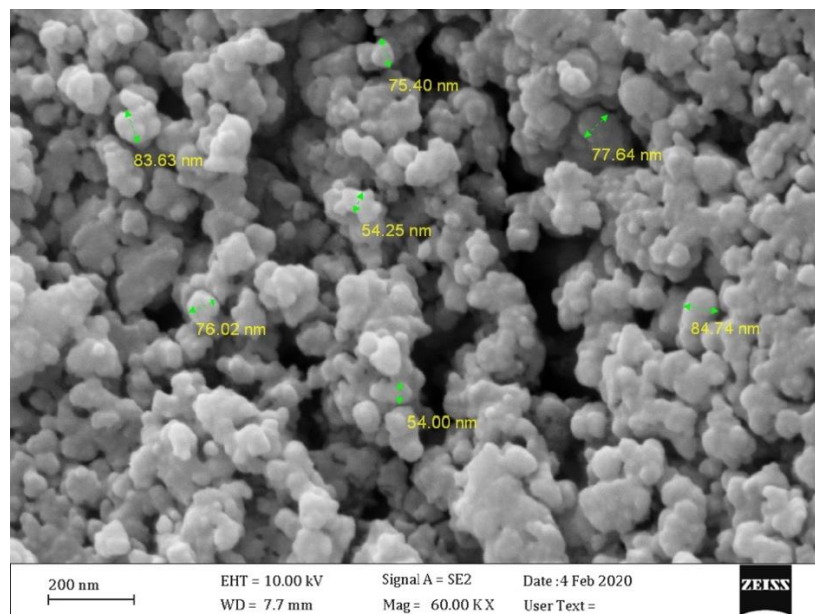


Figure 3

The FESEM image of the SnO₂/ γ -Al₂O₃ catalyst.

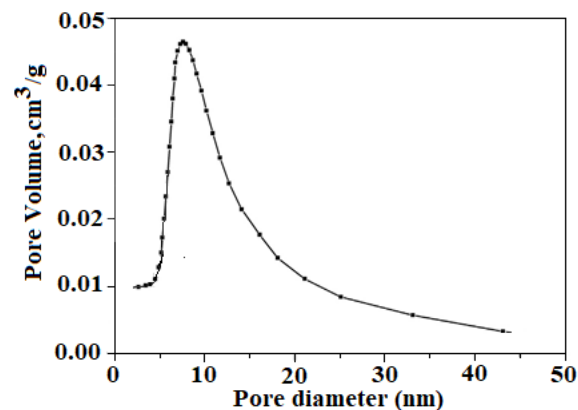


Figure 4

The pore diameter distribution of the SnO₂/ γ -Al₂O₃ catalyst.

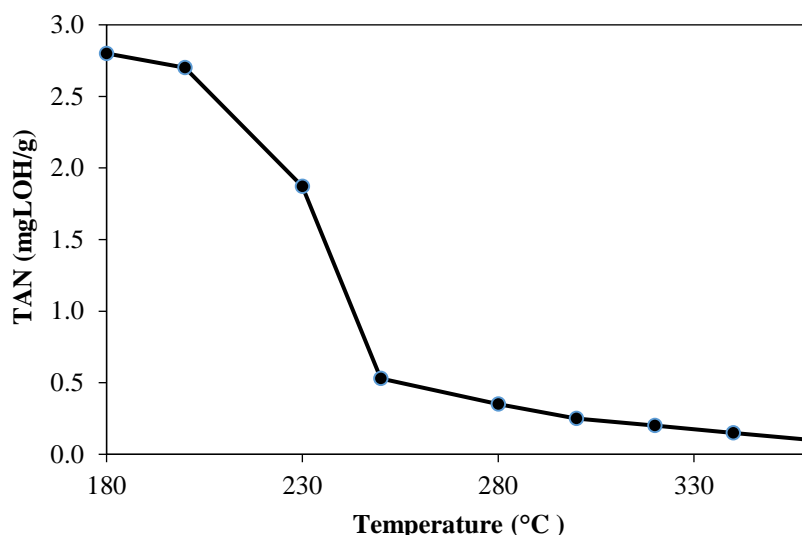
Table 1

Surface area, BJH adsorption cumulative pore volume, and BJH average pore size of SnO₂, γ-Al₂O₃, and SnO₂/γ-Al₂O₃ catalyst.

	S_{BET} (m ² ·g ⁻¹)	BJH adsorption cumulative pore volume (cm ³ ·g ⁻¹)	BJH average pore size (nm)
SnO ₂	16.2	0.07	21.7
γ-Al ₂ O ₃	271.6	0.91	10.2
SnO ₂ /γ-Al ₂ O ₃	213.4	0.54	7.9

3.2. Effect of temperature on esterification reaction

The effect of the reaction temperature on the efficiency of NAs removal from crude oil was investigated, and the results are depicted in Figure 5. It is clear that the total acid number of the crude oil decreased in a temperature range of 200 to 360 °C, so the optimal range of the reaction temperature to remove the naphthenic acids of the crude oil was 250–360 °C, where the TAN declined to less than 0.5 mg KOH/g. Therefore, a reaction temperature of 300 °C was selected as the optimum temperature for further studies. The results are in good agreement with the data on most catalytic esterification processes reported elsewhere (Rana et al., 2018; Wang et al., 2017).

**Figure 5**

The effect of reaction temperature on the total acid number of the crude oil; the initial TAN, the methanol-to-oil ratio, and the reaction pressure were 2.8 mg KOH/g, 2 wt %, and 1 atm respectively.

3.3. Effect of methanol-to-oil ratio on esterification reaction

The effect of different ratios of methanol to oil (M/O) at a temperature of 300 °C and at different velocities of space was investigated. As can be seen in Figure 6, the TAN is lower at an M/O of 2 wt % than an M/O of 1 and 3 wt %. In fact, the methanol-to-oil ratio of 2 wt % exhibited a higher activity compared to the other ratios and was selected as the optimum ratio for further studies and characterizations. Our findings are in good agreement with data reported in the related literature (Wang et al., 2017).

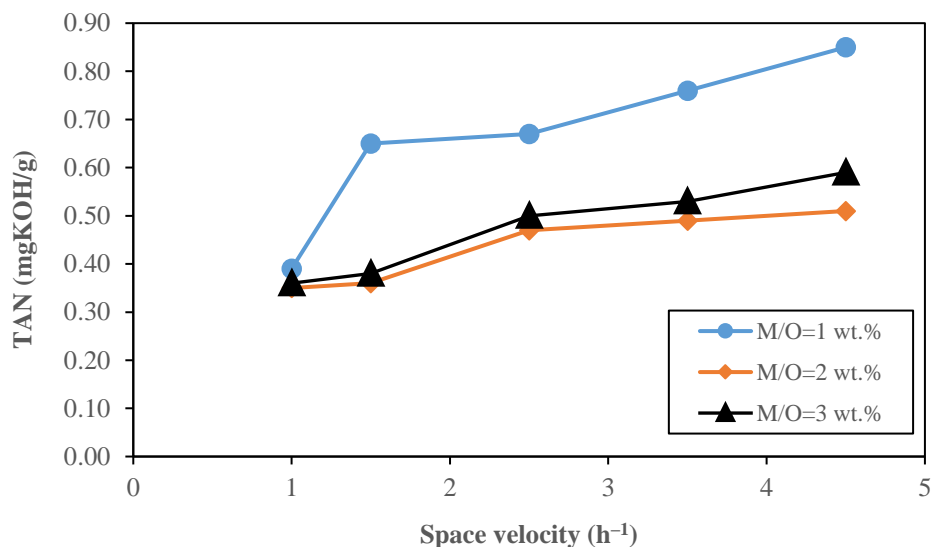


Figure 6

The TAN of the crude oil at different methanol to oil ratios and space velocities; the initial TAN, the methanol-to-oil ratio, the reaction temperature, and the reaction pressure were 2.8 mg KOH/g, 2 wt %, 300 °C, and 1 atm respectively.

3.4. Effect of space velocity on efficiency of NAs removal

Figures 6 and 7 reveal that the TAN of the crude oil increased with enlarging the space velocity. It should be noted that at a high space velocity, the residence time of the reactants is short. When the space velocity was smaller than 2.5 h⁻¹, the total acid number of the crude oil was lower than 0.5 mg KOH/g. Moreover, since a high space velocity indicates less investment and higher production, the optimal space velocity is determined to be 2.5 h⁻¹ (Figure 7).

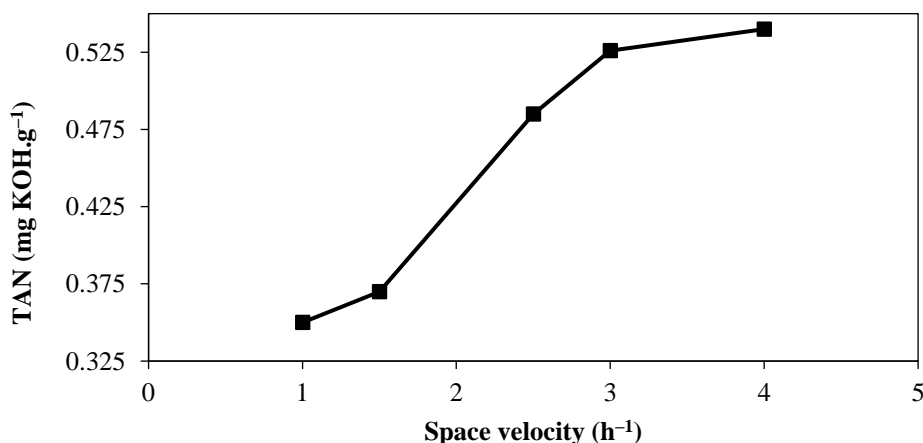


Figure 7.

The total acid number of the crude oil at different space velocities; the initial TAN, the methanol-to-oil ratio, the reaction temperature, and the reaction pressure were 2.8 mg KOH/g, 2 wt %, 300 °C, and 1 atm respectively.

Rana et al. (2018) reported the application of 12-tungstophosphoric acid supported on γ -Al₂O₃ as the catalyst for the removal of naphthenic acids and stated that it could reduce the TAN of crude oil from 2.0 to 0.5 mg KOH/g at a methanol-to-oil ratio of 2 wt %, a temperature of 250 °C, a space velocity of 3 h⁻¹, and a reaction time of up to 100 h. Since the TAN was reduced from 2.8 to 0.5 mgKOH/g in our

study, the $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst shows a higher activity than the $\text{TPA}/\gamma\text{-Al}_2\text{O}_3$ used by Rana et al. (2018). In another work, Wang et al. (2017) reported on microwave-assisted synthesis of ethylene glycol-intercalated Ni–Al Layered double hydroxides (LDHs) and their application in the catalytic esterification of naphthenic acids in crude oil. They reported that the TAN was reduced by 90%.

4. Conclusions

According to the results obtained herein, $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ can be used as a nanocatalyst for the catalytic esterification of naphthenic acids in crude oil. In this context, the space velocity, the reaction temperature, and the ratio of methanol to oil are the important factors influencing this type of reaction. Increasing the reaction temperature to 300 °C causes the esterification reaction to accelerate. However, if the temperature exceeds the optimal value, the esterification reaction slows down. The naphthenic acids of the crude oil declined by 83% at a space velocity of 2.5 h⁻¹, a methanol-to-oil ratio of 2 wt %, and a reaction temperature of 300 °C. Also, in this reaction, the removal of water (as a by-product of the esterification) from the reaction medium helps forward the reaction equilibrium, thereby accelerating the esterification process. The $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ can be a promising catalyst for the esterification of naphthenic acids, so we recommend investigating its performance on a pilot scale so as to advance the development of the industrial process of the removal of naphthenic acids from crude oil.

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Nomenclature

XRD	X-ray diffraction
FESEM	Field emission scanning electron spectroscopy
TAN	Total acid number
BET	Brunauer–Emmett–Teller

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