INTRODUCTION

Shale oil and gas are mainly reserved in low-porosity and ultra-low permeability shale ores. The trillion barrels of shale oil deposits in China offer the potential for less dependence on conventional energy sources.\(^1\)\(^2\) Shale oils located in the Mesozoic and Cenozoic continental sedimentary basins, commonly with low and medium maturity.\(^3\) In contrast to petroleum deposits, these oil shale deposits are characterized by their low fluidity. The polymer-like organics are often referred to as “kerogen,” intimately mixing with inorganic mineral components. However, kerogen contains assortments of complicated compounds that can be converted into petroleum through two primary processes.\(^4\)\(^5\) In
the well-developed surface retorting process, the shale is mined, extracted, and thermally processed to get oil and gas. For in situ conversion, kerogen and bitumen could be transformed underground into a liquid synthetic crude oil, then pumped out to ground, as the feed for upgrading units. 

Compared with North American marine strata, China’s shale oil reveals obviously different characteristics: smaller organic carbon content is generally (−18% vs −35%), lower thermal evolution (Ro is 0.5%-1.1% vs 1.0%-1.7%), higher density of crude oil (above 0.86 g cm−3), and deeply buried (2200-3500 m). Meanwhile, the content of brittle minerals is high (50%-70%), and clay mineral content is elevated (30%-50%). It can be found from the "pyramid" distribution of liquid hydrocarbons; the low-medium matured shale oil is an ultra-heavy unconventional resource, and the organic phase would be undergoing a conversion sequence of kerogen to asphalt then to shale oil. 

In situ conversion process (ICP) and upgrading process (IUP) are widely used for decades. Typically, heater cables increase temperatures throughout the entire reservoir, then hydrocarbons are extracted from immatured kerogen-rich shale or bitumen. In this way, a reservoir “driving force” is generated, and rejuvenate production in depleted field can be attained under some situations. These in situ technologies enhance hydrocarbon recovery, reduce or eliminate diluted consumption, and lessen environmental impacts. Green River oil shale in situ conversion has been carried out under N2–H2O and CO–H2O for up to 28 days at temperatures in the range of 280-370°C. A wide range of researches have been carried out by academia and industries. Shell in situ conversion process, a highly novel approach of in situ retorting, converts the kerogen to gas and petroleum-like liquids, and makes it able to obtain desirable petroleum products more efficiently. Exxon mobile Foundry in situ upgrading process uses salamander heaters to initiate thermal cracking of heavy oil and/or bitumen in place. 

Acid and/or bifunctional catalysts have been employed to promote in situ upgrading. Catalytically enhanced oil recovery technologies stem from Canadian oil sands bitumen exploration. Simultaneous recovery and downhole upgrading of the extra-heavy oils have been investigated from a decade ago. Some liquid acids, organometallic complex, or NiMo and CoMo catalysts have been applied for the heavy oil in situ upgrading in pilot plant and demonstrated application. Certain numbers of zeolites, solid super acids, and dispersed transition metals or metal oxides nanoparticles have been tested for their cracking activity in laboratory scale. Up to date, shale oil in situ catalytic upgrading faces two main barriers when it is compared with oil sands bitumen upgrading. These are (a) shale oil occurs in solid rather than in viscous liquid, and (b) shale oil initially has a high low permeability. It is vital to design and develop tailored catalysts that can enhance downhole upgrading of semi solid oil and improve its mobility under moderate conditions. 

Evolution of underground hydrocarbon generation in shale oil follows a complex process in which the low matured organic compounds, mainly kerogen, are decomposed into bitumen, and the bitumen is further converted to oil and gas via visbreaking or cracking. The conventional heterogeneous catalysts have poor applicability to shale oil conversion and upgrading for their poor downhole stability. It is critical to design and fabricate high-efficient catalysts to facilitate in situ upgrading of medium-low matured shale oil. 

Natural zeolite-based aluminosilicates reveal good hydrothermal stability, have been applied for bitumen and bio-oil in situ upgrading, and showed the good performance on oil yield under subcritical water. Clinoptilolite-based porous aluminosilicates were prepared for shale oil upgrading approach. 

In this study, microporous and mesoporous aluminosilicates were firstly used for in situ conversion of low and medium matured shale oil in Sinpec patented hydrocarbon generation and expulsion unit. Natural zeolite-based catalysts initiated this “shale oil to hydrocarbons” process below 350°C. Al-SBA-15 catalysts were synthesized and showed high activity and good stability. These catalysts were evaluated for shale oil in situ upgrading experimentally for 48 hours reaction. Pyrolysis kinetics, shale oil conversion, and oil production and gas yields were studied. The feasibility of the porous aluminosilicates for shale oil catalytic conversion provides a new approach for shale oil exploration.

### 2 | CATALYSTS PREPARATION

#### 2.1 | Microporous catalysts

H-clin and Ni-clin catalysts have been prepared by ion exchange method. The natural zeolite used in this study was purchased from Laixi mine, with Si/Al ratio of 3-4.

The synthesis of H-clin consisted of the following steps: The natural zeolite was immersed in 0.5 mol L−1 HCl solution at a solid–liquid ratio of 1:5 (g mL−1) under ultrasound (power 70%) at 70°C for 2 hours. Impregnated zeolite was washed with deionized water for 3 times and dried in bake oven at 120°C for 10-12 hours. After ultrasound (power 70%) at 70°C for 2 hours with 1 mol L−1 NH4Cl, it was washed with deionized water for several times, and dried in bake oven at 120°C for 10-12 hours. The above processes were repeated twice. The dried zeolite was calcined in muffle furnace at 450°C for 2 hours, and H-clin was synthesized.

Transition metal oxides showed good deoxygenation activity for the fatty acid and ester in the reaction of liquefied bio-oil. In this study, Ni salts were selected as precursor and Ni-clin catalyst was prepared by impregnation–precipitation
method. NiO nanoparticles were precipitated with 1 mol L⁻¹ NiSO₄ and ammonia at pH 10. The H-clin and solution prepared above were mixed at a solid–liquid ratio of 1:5 (g mL⁻¹) under ultrasound (power 70%) at 60°C for 2 hours. The product was washed with deionized water for several times and dried in oven at 120°C for 10-12 hours, calcined in muffle furnace at 450°C for 2 hours, and Ni-clin was synthesized. Figure 1 showed the EDAX mapping images on Ni-clin surface; the content of Al was low and Ni was distributed uniformly.

2.2 Mesoporous catalysts

Al-SBA-15 catalysts were synthesized by following one-step crystallization procedure.

1.8 g of PEO-PPO-PEO (P123) was dissolved in 65 mL deionized water, stirring at room temperature until a clear liquid A was obtained. A certain amount of acid solved clinoptilolite and Al₂(SO₄)₃ as the liquid B. The liquid A was added with liquid B with vigorously magnetic stirring at room temperature for 2-3 hours, and the mixture was drop-added with a certain amount of tetraethyl orthosilicate (TEOS) with Si/Al ratio of 5 or 10, and stirred at room temperature for 3-4 hours, then stirred at 40°C for 36 hours. The obtained gel was aged at 40°C in a Teflon-lined steel autoclave, then crystallized at 120°C for 48 hours in vacuum drying oven. Then, the solid product was filtered, dried at 100°C for 4 hours. After calcining at 550°C for 6 hours (heating ramp of 10°C min⁻¹ to 550°C), Al-SBA-15(5) and Al-SBA-15(10) were synthesized.

Figure 2 presents the N₂ isotherms and pore size distribution of the Al-SBA-15 catalysts. The typical hysteresis loop showed that both catalysts existed mesoporous structures. The isotherm with a sharp jump at 0.7-0.8 relative pressures indicated that the catalysts had regular mesoporous structure, and pore sizes centered at 6.25 and 8.53 nm, respectively. Physical characters of the catalysts are listed in Table S1.

Figure 3 illustrates the FT-IR spectra and TEM images of Al-SBA-15 catalysts. All peaks at 460, 808, 1080 cm⁻¹ were attributed to the bending vibration of Si-O, the intrinsic Si-O symmetric stretching vibration, and the asymmetric Si-O-Si. There was a wider transmission peak at 2430 cm⁻¹, which was the stretching vibration peak of carbon dioxide. Boccuti believed that the transmission peak near 960 cm⁻¹ was related to the stretching vibration of Si-O-M, so the peak near 960 cm⁻¹ can be used as a criterion to judge whether Al entered the framework of molecular sieves. Al-SBA-15 catalysts exhibited peaks near 960 cm⁻¹, which indicates that the Al entered the framework of molecular sieves. With the increase of Si/Al ratio, the peak strength deduced because of the decrease of Al content in the skeleton. Both catalysts had a regular mesoporous structure in vertical and parallel directions, which indicated that the introduction of Al would not destroy the well-defined structure of SBA-15. The prepared catalysts also had highly ordered two-dimensional hexagonal structure, which was consistent with XRD patterns.

3 PYROLYSIS KINETIC STUDY OF SHALE OIL

The pyrolysis study is a simple and accurate experimental method for studying the thermal conversion characteristics of raw materials. It was carried out on a thermogravimetric (TG) instrument at a specific heating rate. In this paper, the pyrolysis characteristics of shale oil thermal and catalytic conversion were studied on TA449C (NETZSCHS). H-clin, Ni-clin, Al-SBA-15(5) and Al-SBA-15(10) were mixed with raw shale powder, respectively. The kinetic analysis was carried out by Coats Redfem method and Starinkequal conversion rate method to investigate the pyrolysis characteristics of organic matter decomposition. The reaction activation energy and characteristic parameters were used for optimizing the catalytic conversion
conditions of shale oil conversion to hydrocarbon and in situ upgrading.

The pyrolysis kinetics analysis was performed using the basic rate equation (Equation 1) by selecting the nonisothermal kinetic data of the thermal decomposition.

\[ \frac{da}{dt} = K f(\alpha) \]  

where \( \alpha \) — conversion, %; \( K \) — Arrhenius constant; \( f(\alpha) \) — Kinetic function.

From Arrhenius equation (Equation 2)

\[ K = A \exp \left( -\frac{E}{RT} \right) \]  

Supposing \( f(\alpha) \) is only related to \( \alpha \), \( f(\alpha) \) can be expressed as:

\[ f(\alpha) = (1 - \alpha)^n \]  

where \( n \) is the reaction order.

Substituting Equations (2) and (3) into Equation (1), get Equation (4)

\[ \frac{da}{dt} = A \exp \left( -\frac{E}{RT} \right) (1 - \alpha)^n \]  

The heating rate \( \beta \) is defined as

\[ \beta = \frac{dT}{dt} \]  

Substituting Equation (4) into Equation (5)

\[ \frac{da}{dt} = \frac{A}{\beta} \exp \left( -\frac{E}{RT} \right) (1 - \alpha)^n \]  

Equation (6) is the kinetic equation of pyrolysis.

For the separation of variables in Equation (6), Equation (7) was obtained

\[ \frac{da}{f(\alpha)} = \frac{A}{\beta} \exp \left( -\frac{E}{RT} \right) dT \]
The corresponding functional form of the reaction with known reaction mechanism can be used to integrate or differentiate it, and then map to $1/T$. According to the fitting curve of the graph, the reaction mechanism of the reaction can be obtained.

\[
\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT}
\]

Figure 4 illustrates the TG and DTG curves of shale oil thermal and catalytic pyrolysis at atmospheric pressure. The TG curve of each sample shows only one maximum weight loss rate $D_{\text{max}}$, indicating that the pyrolysis parameters of these samples can be obtained according to the single-zone calculation. Al-SBA-15(5) showed the similar TG curve as Al-SBA-15(10), so its catalytic pyrolysis has not been covered by the following kinetic analysis. As shown in Figure 4, the temperature $\theta_{\text{max}}$ (corresponding to the maximum weight loss rate $D_{\text{max}}$) of shale oil pyrolysis was decreased with catalysts addition. Al-SBA-15(10) reduced $\theta_{\text{max}}$ about 100°C while H-clin and Ni-clin catalysts only decreased $\theta_{\text{max}}$ less than 10°C.

The shale oil pyrolysis conforms to the first-order reaction model in the corresponding temperature range for each sample, and the activation energy $E_a$ of the pyrolysis (including catalytic pyrolysis) reaction is calculated after fitting the nonisothermal data, as shown in Tables 1 and 2. It is noticed that Al-SBA-15 catalyst reduced the effluent temperature of the volatiles by nearly 50°C. It confirmed that the addition of acidic mesoporous catalyst can initiate the conversion of shale oil to hydrocarbons at a lower temperature regime.

It is generally believed that the pyrolysis process of immature kerogen in shale is a two-stage decomposition. The first stage is the pyrolysis of kerogen to form bitumen where the pyrolysis temperature is lower than 300°C and the reaction rate is faster. The second stage is bitumen decomposition to produce light oil, gas, and residual carbon, and this stage has a higher pyrolysis temperature and a slower reaction rate, which is a rate limiting step of pyrolysis of immatured organic matter. Therefore, the main result of catalyst addition is promoting cracking of bitumen to oil and gas.

Starinkequal conversion rate method can be used to calculate kinetic parameters without model assumptions. In the range of 400-500°C, deducing from TG and DTG parameters, the activation energy $E_a$ of shale oil noncatalytic pyrolysis is 113.80 kJ mol$^{-1}$ that is consistent with the literature reported $E_a$. The activation energy $E_a$ was reduced to approximately 50 kJ mol$^{-1}$ on microporous catalysts, H-clin and Ni-clin, and 40 kJ mol$^{-1}$ on mesoporous catalyst Al-SBA-15 (10). Combining the calculation results of the pre-exponential factor $A$ with the stage weight loss, it can be deduced that in the tested temperature range, the thermal conversion of low activation energy $E_a$ can only made a small amount of easily converted components decomposed, which illustrated as lower $\theta_{\text{max}}$. The catalyst injection makes the more heavy ingredients transformed into oil and gas with elevated $D_{\text{max}}$ and decreased $\theta_{\text{max}}$, which leads to milder reaction conditions for shale oil conversion. This indicates that the conversion conditions of shale oil are milder with the acidic catalysts, and such catalysts can reduce the in situ pyrolysis temperature of shale oil and promote the energy efficiency of exploration.

4 | SHALE OIL CATALYTIC CONVERSION ACTIVITY EVALUATION

In order to compare the hydrocarbon generation and expulsion activity of the catalysts, shale oil conversion and in situ upgrading experiments were carried out in the Sinopec patented DK-II unit (Figure S1). The catalyst was injected to the unit, and the experiment was done under artificial maturation conditions to simulate the kerogen and bitumen evolution. The low matured shale oil was heated for 48 hours, and the total amount of produced oil and gas was gathered.
for analysis. The conversion efficiency of the shale oil and the derived bitumen was investigated intensively.

### 4.1 Shale oil catalytic conversion experiments

In this experiment, the total organic carbon of the ore samples was 17.89%, and the oil content was 10.5%. The catalyst includes two kinds of microporous catalysts, H-Clin and Ni-Clin, and two mesoporous catalysts, Al-SBA-15 (Si/Al = 5) and Al-SBA-15 (Si/Al = 10). Considering the thermochemical reduction (TSR) of sulfate, MgSO₄ was chosen as a catalyst for simulating the action of TSR, and the catalytic effect was compared with the porous aluminosilicate catalyst. The experimental sample was crushed shale particles (size 1-2 mm), and the mass ratio of the reactants was: rock sample: water: catalyst = 100:10:1.

The experiment was carried out in the hydrocarbon generation and expulsion simulation experimental device. The shale ore thermal compression simulates the process underground 1500 m circumstances. The rock density is 2 kg m⁻³, that is, the overlying ore pressure is 30 MPa and the fluid pressure is up to 15 MPa. The experiment was heated to 350°C at a heating rate of 0.2°C min⁻¹ and maintained the temperature for 48 hours. After the conversion process, the oil and gas discharged from the shale were collected, and the oil, gas, and solid residual were tested and analyzed to get mass balance and chemical compositions identification. The gaseous product was tested by gas chromatography Agilent GC 6890 to quantify the components. The ratio of saturated hydrocarbons, aromatic hydrocarbons, and asphaltene was elucidated by classical oil fractionation. SARA method (Fan et al, 2002) was performed with regard to the polarity of these fractions by using different solvents and adsorbents. The solid residual was analyzed by Rock-Eval pyrolysis.

### 4.2 Catalytic activity

Rock-Eval pyrolysis is used to identify the type and maturity of organic matter, and to detect petroleum potential in sediments. Shale residue was obtained after 350°C conversion, and submitted for Rock-Eval pyrolysis analysis. The hydrocarbon generation efficiency was calculated as Equation (9).

\[
G_1 = \frac{[(S_1 + S_2)_{ore} - (S_1 + S_2)_{residue}]}{(S_1 + S_2)_{ore}} \tag{9}
\]

where \(S_1\) stands for free hydrocarbon in the ore, \(S_2\) stands for petroleum generation potential, \(S_1 + S_2\) accounts for the total hydrocarbon generation potential when the ore was pyrolyzed.

For oil and gas products, hydrocarbon generation efficiency can be expressed as:

\[
G_2 = \frac{\text{expulsed oil + remaining gas and oil}}{(S_1 + S_2)_{ore}} \tag{10}
\]

Theoretically, \(G_1\) has the same value of \(G_2\). As far as the different experimental conditions between Rock–Eval pyrolysis and the hydrocarbon generation and expulsion experiment, there are inevitably weight loss in the collection of oil and gas products, especially the hydrocarbon with the carbon number less than 12. So here in this paper, \(G_1\) is used to evaluate hydrocarbon generation efficiency.

Figure 5 shows the hydrocarbon generation efficiency calculated according \(G_1\) as the sequence: mesoporous catalyst Al-SBA-15 (Si/Al = 5, Si/Al = 10) > microporous catalyst (H-clin, Ni-clin) > Inorganic salt catalyst (MgSO₄) > aqueous pyrolysis > anhydrous pyrolysis. It can be seen that the hydrocarbon generation efficiency of the ore without water is only 10.89%, and the addition of 10 wt% water acts as a hydrogen donor, so that the efficiency is 1.5 times that of the case without water. The \(G_1\) of the samples with the catalyst addition was further improved, and the increase rate was 2%-16%. The \(G_1\) on Al-SBA-15 (Si/Al = 5) is up to 32.67%, twice as the \(G_1\) of the ore with water and without the catalyst.

After the experiment, the residual bitumen in the ore sample was extracted, and the mass percentage of residual bitumen under different catalytic conditions was calculated and

### TABLE 1 Characteristic weight loss (%) of various samples (at a heating rate of 10°C min⁻¹)

| Sample                  | \(D_{max}\) (%) | \(\theta_{max}\) (°C) | \(T_s\) (°C) |
|-------------------------|-----------------|------------------------|-------------|
| Without catalyst        | 0.104           | 457                    | 285         |
| With H-clin             | 0.193           | 451                    | 292         |
| With Ni-clin            | 0.228           | 451                    | 300         |
| With Al-SBA-15(10)      | 0.168           | 355                    | 232         |

### TABLE 2 Kinetics parameters of various samples decomposition

| Sample                  | \(E_a\) (kJ mol⁻¹) | A (min⁻¹) | Temperature zone (°C) |
|-------------------------|--------------------|-----------|-----------------------|
| Without catalyst        | 113.80             | 9.52 × 10¹² | 390-520               |
| With H-clin             | 50.98              | 2.30 × 10¹² | 400-500               |
| With Ni-clin            | 51.32              | 1.18 × 10¹³ | 400-500               |
| With Al-SBA-15(10)      | 37.28              | 1.56 × 10¹³ | 280-420               |
divided by the hydrocarbon generation efficiency to get the residual pyrolyzed bitumen rate. This rate is defined to qualify the amount of converted bitumen that has not converted to light oil and gas. According to the kinetic analysis of shale oil pyrolysis under atmospheric pressure, it can be seen that the catalyst reduces the activation energy \( E_a \) of organic matter conversion in shale by promoting the secondary pyrolysis—bitumen cracking to oil and gas. The thermal sulfate reduction (TSR) of MgSO\(_4\) has no obvious effect on improving the \( G_1 \) hydrocarbon generation efficiency or promoting the secondary cracking of bitumen, and the water solubility of the inorganic salt causes the salt—oil separation problem in the subsequent oil collection and processing. MgSO\(_4\) is not a suitable catalyst for in situ upgrading of low and medium matured shale oil.

As far as gas production rate was concerned in Figure 6, the Al-SBA-15(5) and Al-SBA-15(10), especially Al-SBA-15(5), have obvious enhancing effect on gas production. It greatly increases the production of gaseous hydrocarbons, helps to maintain formation pressure, prevents the invasion of surrounding formation water, and promotes the oil production and improves the ultimate hydrocarbon recovery. The microporous catalyst (H-clin, Ni-clin) reduces the gas production rate. One possible reason is that there are fewer accessible active sites on the microporous catalysts for the relatively large molecular-sized bitumen compounds. Secondary decomposition of bitumen to gas and oil would be lessened on H-clin and Ni-clin.

5 | CONCLUSIONS

1. The microporous catalysts, H-clin and Ni-clin, were prepared by natural clinoptilolite exchange and impregnation—precipitation respectively. Al-SBA-15 catalysts were prepared by one-step crystallization method,
taking inorganic aluminum salt as the aluminum source, adding the templating agent, mixing Al source and Si source, aging, drying and calcination to synthesize acidic, hydrothermally stable catalysts.

2. Atmospheric pyrolysis kinetics show that the catalysts can reduce the activation energy $E_a$ of organic matter conversion in shale. Al-SBA-15 catalyst declined $E_a$ of organic matter conversion in shale from 113.80 kJ mol$^{-1}$ to 37.28 kJ mol$^{-1}$, thereby reducing the pyrolysis temperature of shale oil, increasing the pyrolysis rate, reducing the severity of in situ upgrading of low and medium matured shale oil.

3. The shale oil catalytic conversion evaluation showed that the catalyst improves the hydrocarbon generation conversion rate of organic matter in shale oil, by promoting the secondary cracking of pyrolyzed bitumen, improves the quality of produced oil, increases the gas production, and enhanced oil and gas recovery.

4. Porous aluminosilicates demonstrate good catalytic activity, especially mesoporous catalyst Al-SBA-15 (Si/Al = 5), which showed the best performance in hydrocarbon generation efficiency, promote secondary cracking of pyrolysis asphalt, increase hydrocarbon gas production.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section.

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