Recent Progress on In Situ Catalytic Conversion Catalysts for Oil Shale

Aibin Wu,[⊥] Junwen Wu,* Liu Chen,[⊥] Jianzheng Su, and Weichu Yu*

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ABSTRACT: With the gradual depletion of oil resources, it is urgent to vigorously develop unconventional and renewable energy sources. As an unconventional resource with abundant resources, the rational and efficient development of oil shale is of great significance to alleviating the national energy crisis. The main methods of oil shale development are surface dry distillation and in situ transformation. In situ catalytic conversion technology, as an emerging mining method, has the potential to improve efficiency, reduce costs, and environmental impact and is an important direction for future oil shale development. As a key component in the in situ conversion process, catalysts play a crucial role in the rate, selectivity, and product quality of the reaction. However, the research on oil shale pyrolysis catalysts is still in the laboratory

stage and is difficult to translate into practical applications. Therefore, this paper reviews recent progress of catalyst research in the in situ catalytic conversion of oil shale, including the types, design principles, and reaction mechanisms of catalysts, and looks forward to the future development direction. It provides a certain reference for the discovery of new catalysts that can improve yield and reduce environmental pollution in the process of oil shale extraction and also provides a valuable technical reference for the green development and utilization of unconventional and strategic alternative energy sources in the world and the transformation and sustainable development of the global energy structure.
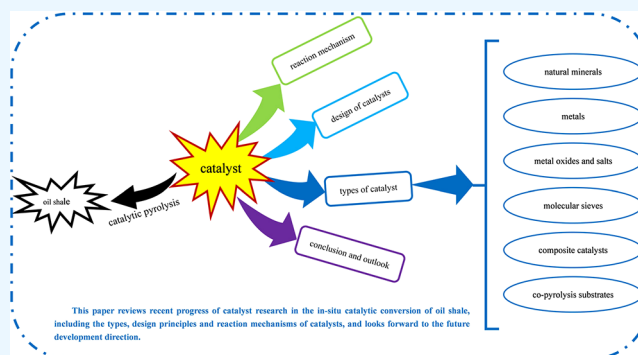
1. INTRODUCTION

Oil shale is a sedimentary rock containing solid organic matter within an inorganic mineral framework.[1−3] Its world resource reserves are extremely abundant, with a total amount of $100,000 \times 10^8$ t.[4] The potential shale oil resources exceed $4,000 \times 10^8$ t, which is more than the world's total crude oil resources.[5−8] The distribution of the world's oil shale resources is relatively uneven, mainly concentrated in the United States, Russia and China, with the resource reserves and potential shale oil reserves accounting for 90% and 80% of the world's, respectively.[9−12] Oil shale in China is mainly distributed in the eastern, central, and Qinghai-Tibetan regions, accounting for 48%, 22% and 17% of the total national resources, respectively. The resources in the western and southern regions are relatively small.[2,3] The rich and relatively concentrated nature of its resources reserves make oil shale have enormous potential as an alternative energy source.[13−15] China's oil reserves are scarce, and currently, a large amount of oil relies on imports. Therefore, vigorously developing and utilizing oil shale is beneficial for alleviating China's energy crisis.

Oil shale is a special type of unconventional resource. Its organic matter, kerogen, is completely solid in its natural state and cannot be extracted like natural gas or oil in reservoirs. When heated to 450∼550 °C under isolated air or inert atmosphere conditions, organic matter gradually cracks to form shale oil, while solid shale char, shale gas and water are generated.[16]

The two main methods for extracting oil shale are surface distillation[17,18] and in situ conversion technology.[19,20] Ground dry distillation, a well-established technology, is suitable for developing near-surface or shallow oil shale reserves. However, this method of extracting rocks to the ground has great limitations, facing problems such as high development costs, large land occupation and environmental pollution.[21,22] Underground in situ conversion mining technology is a development method that involves artificially heating underground oil shale reservoirs, cracking solid kerogen inside the oil shale into oil and gas in situ, and then extracting it to the surface through certain process.[23−27] At present, this technology has not yet reached the level of industrial

development, but when mature, it has the advantages of green environmental protection, small land occupation, low development costs, and the development of deep oil shale resources, which is an inevitable trend for future oil shale extraction.

The traditional in situ extraction method for oil shale involves heating the oil shale formation using different heating methods to pyrolyzed the kerogen in the oil shale into shale oil and gas.[27] In practical application, the activation energy required for the decomposition of solid organic matter in oil shale is relatively high, resulting in its cracking requiring relatively high temperatures, usually exceeding 500 °C, leading to high energy consumption. Furthermore, the products of thermal cracking are prone to dehydrogenation reactions, generating a large amount of semi coke products, which results in few light fractions in oil shale oil and relatively poor product quality. Experiments have shown that the use of catalysts can reduce the cracking temperature of kerogen, improve in situ conversion efficiency and oil quality, which is an effective way to reduce mining costs and increase recovery rates.[28,29] Therefore, adding catalysts in the process of oil shale extraction can effectively reduce the energy required, save resources, and improve product quality.

In addition, there are many auxiliary methods for in situ pyrolysis of oil shale, such as using organic solvents extraction,[30] subcritical water extraction,[31,32] critical water extraction[33] etc. This paper mainly reviews the relevant research on catalysts for in situ catalytic pyrolysis of oil shale, so we will not delve too much into them here.

2. REACTION MECHANISM

Taking the Green River oil shale as an example, the pyrolysis process of oil shale is shown in Figure 1 and 2, which is divided
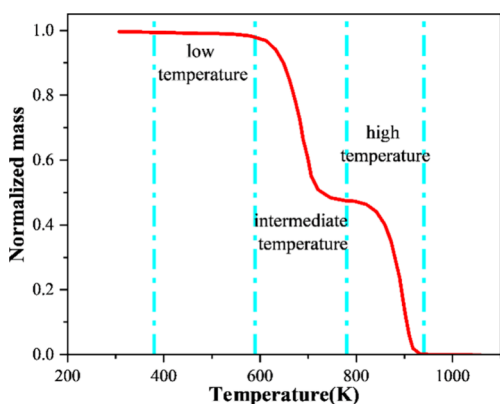

Figure 1. TGA of Green River oil shale.[34] Reprinted in part with permission from ref 34. Copyright 2010 American Chemical Society.

into three stages: low temperature, medium temperature and high temperature.[34] In low temperature stage, the gases and water adsorbed on the surface of the oil shale are removed. At medium temperature, organic matter kerogen in oil shale decomposes to produce oil and gas. While at high temperature, inorganic minerals in oil shale begin to decompose and be discharged.[35−37] Therefore, the pyrolysis of organic matter kerogen in oil shale is considered to be the main process of oil shale pyrolysis.

Kerogen is a complex organic polymer with diverse structures and compositions; therefore, there is no fixed and unified chemical structure for kerogen. The configuration of

the kerogen molecule determines the quality of its pyrolysis product as well as the amount generated, so many researchers have used various characterization methods and molecular simulation computational techniques to study its structure. These research found that it was mainly composed of five elements: C, H, O, N and S,[38] which could not be dissolved in general organic solvents.[39] Moreover, the molecular configuration of kerogen in different regions was quite different, as shown in Figure 3, so it was of great significance to study the pyrolysis mechanism of kerogen from the structure.

As shown in Figure 2, the pyrolysis of kerogen is mainly concentrated in the medium temperature stage, which can be divided into two stages: the first stage is the initial pyrolysis of kerogen, which transforms into asphalt (mainly composed of alkanes, carboxylic acids, phenols, and esters[40]) and a small amount of shale oil. Free radicals begin to form, and oxygen-containing functional groups such as carboxyl, alcohol, hydroxyl and carbonyl groups begin to appear. The second stage involves further pyrolysis of the intermediate product asphalt, generating a large amount of shale oil and pyrolysis gas.[16,41,42] During the cracking process, C−C, C−H and C−O bonds break, producing highly reactive free radicals that combine to form combustible gases and shale oil. The generation, exchange and consumption of free radicals are considered to be the major steps in the pyrolysis process of oil shales.[43−45]

In order to further study the pyrolysis mechanism of kerogen, many studies have been carried out on its structure. It is found that pyrolyzed asphalt is an intermediate produced in the pyrolysis process of kerogen, which maintains the basic three-dimensional structure of kerogen and has similar carbon content and chemical structure.[43] Therefore, the follow-up researchers constructed a representative molecular model of kerogen and then used these average molecular structures to calculate and analyze the reaction sites and pyrolysis behavior by constructing two-dimensional (2D) and three-dimensional (3D) reaction models of kerogen, and put forward the pyrolysis theory of kerogen.[43,48−50] As shown in Figure 4, the pyrolysis of kerogen was divided into two stages; the first stage was that the weaker chemical bonds first form aliphatic hydrocarbon structures, i.e., *n*-alkanes, isoparaffins, and alkenes. Zhang[51] analyzed more than 500 kerogen species in different chemical environments and found that the bond dissociation energy trends of each type of bond follow C−S < C−N < C−O < C−C < C−H < C=C. The second stage was the aromatic alkylation reaction, in which the broken kerogen fragments pyrolyzed, mainly involving the substitution of aromatic structures with hydrocarbons, long linear hydrocarbons, and cyclic hydrocarbons. Compared with the first stage, the products in this possess had a higher degree of stability.

Therefore, the addition of catalysts in the pyrolysis process of kerogen can promote the cracking of long-chain hydrocarbons into low molecular weight hydrocarbons, thereby increasing the production of light oil products.[52,53]

3. DESIGN OF CATALYSTS

In the in situ catalytic conversion process of oil shale, the addition of catalysts can significantly improve the yield and quality of shale oil and reduce energy consumption. The composition and morphology of the catalysts, active sites, surface properties and the interaction mechanism between catalysts and substrates can affect the efficiency of in situ
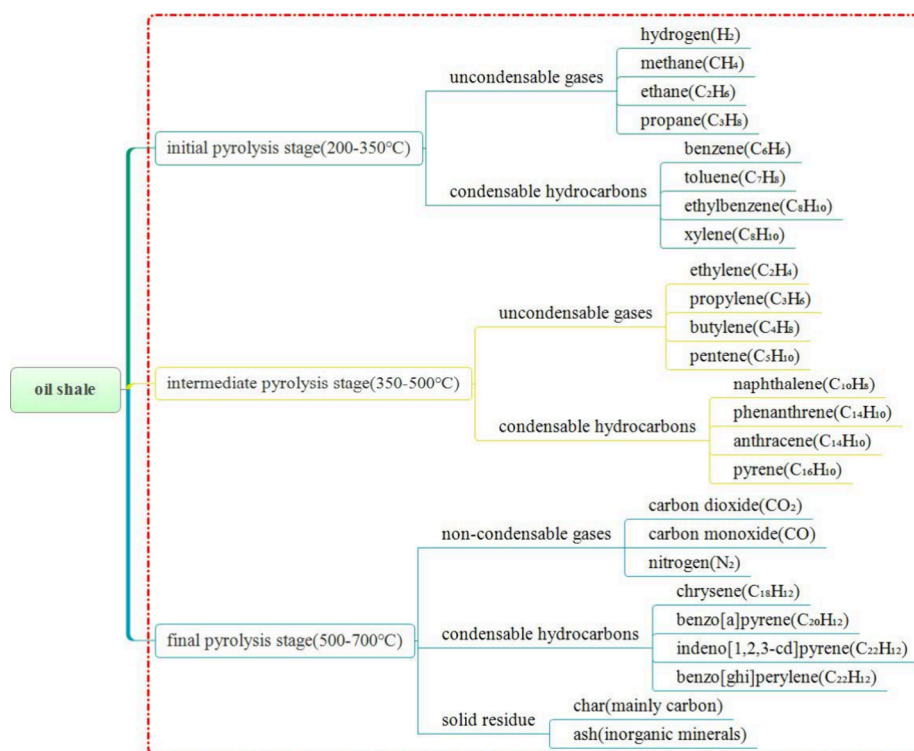
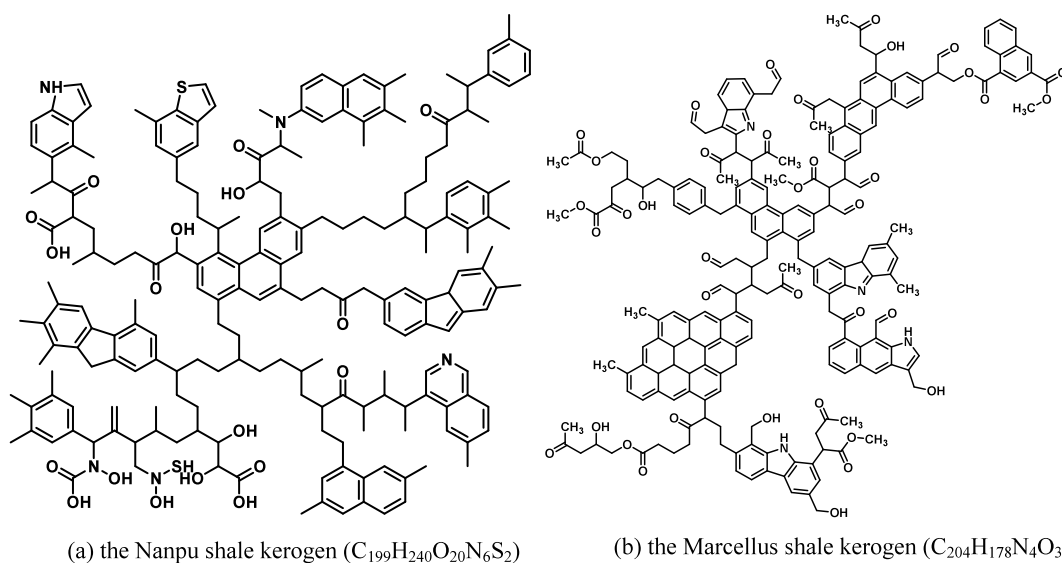**Figure 2.** Distribution of oil shale pyrolysis products.

(a) the Nanpu shale kerogen ($C_{199}H_{240}O_{20}N_6S_2$)   (b) the Marcellus shale kerogen ($C_{204}H_{178}N_4O_{38}$)

Figure 3. 2D chemical structure of kerogen:[46,47] (a) the Nanpu shale kerogen ($C_{199}H_{240}O_{20}N_6S_2$). Reprinted in part with permission from 47. Copyright 2023 Elsevier Ltd. (b) Marcellusshale kerogen ($C_{204}H_{178}N_4O_{38}$) . Reprinted in part with permission from ref 46. Copyright 2021 Elsevier B.V.

pyrolysis and the quality of the products.[54−57] The catalyst used is generally composed of active components and carrier materials, among which the active components include metals and oxides, while the carrier materials are commonly porous materials such as molecular sieves, alumina, and shale ash. The composition and morphology of catalysts can affect the density and surface area of their active sites.[58,59] A catalyst with good performance should have a larger surface area and regular pore size, which can give the catalyst more active sites and promote the progress of the reaction.

In the in situ catalytic pyrolysis of oil shale, catalysts can be divided into natural minerals, metals, metal oxides and salts, molecular sieves, copyrolysis substrates, and composite catalysts, which have different roles in the in situ catalytic pyrolysis process, as shown in Table 1.

The catalytic mechanism of metals is to affect the configuration and distribution of electrons on the surface of kerogen, thereby accelerating the rate of charge transfer between C−C bonds, resulting in the cleavage of kerogen molecules.[60] Catalysts rich in active acid sites, such as Lewis acid and Brønsted acid, can trigger the cracking of alkanes and
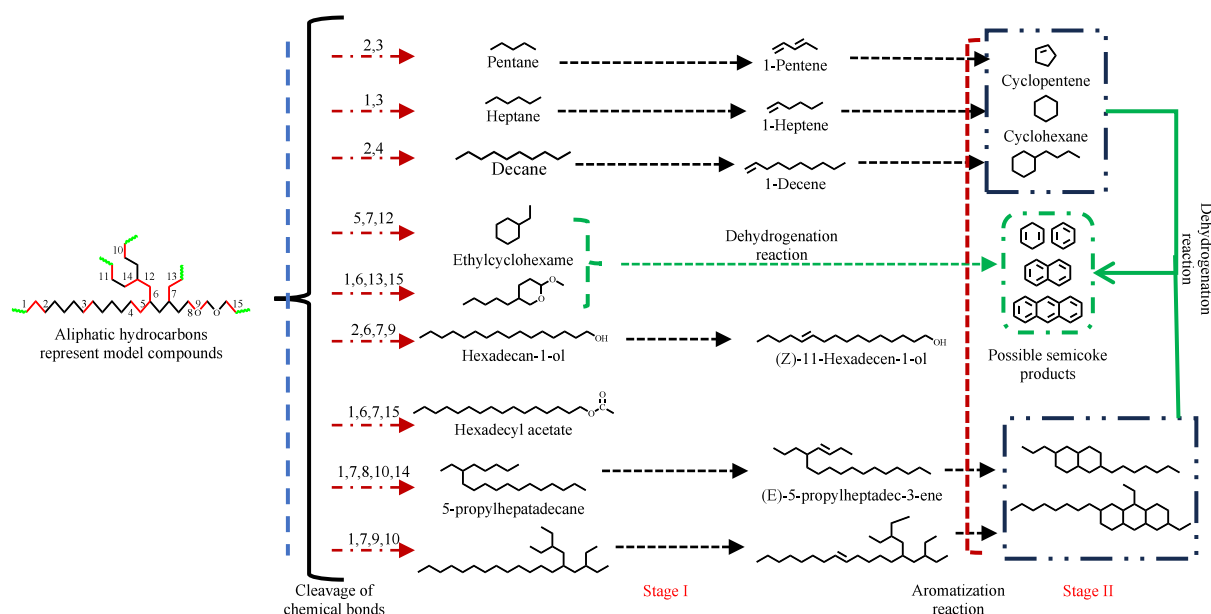
Figure 4. Mechanism of organic matter kerogen pyrolysis.[48] Reprinted in part with permission from ref [48]. Copyright 2021 Elsevier B.V.

Table 1. Catalytic Performance of Partial Oil Shale Catalysts

Type of catalyst	Name of the catalyst	Catalytic performance	Percentage of reduced activation energy[a]	Reference No.
Natural minerals	Silicate	Natural minerals tend to direct hydrocarbons from kerogen to low molecular weight hydrocarbons (C_7–C_{12}), where the addition of silicates promotes the increase of aliphatic hydrocarbons in the product, while carbonates promote the formation of aromatic hydrocarbons.	25.44%	62
	Carbonate		−5.02%	62
Metals	Co	It affects the configuration and distribution of electrons on the surface of kerogen, thereby accelerating the charge transfer rate between C−C bonds, promoting the cleavage of kerogen molecules.	--	72
	Ni		--	73
Metal oxides and salts	$CoCl_2·6H_2O$	It with high activity can act as activation centers to accelerate the cleavage of chemical bonds in organic matter, including the cleavage of long-chain alkanes, the aromatization of alicyclic compounds, and the cleavage of heterocyclic compounds.	26.69%	52
	$MnSO_4·H_2O$		21.49%	52
Molecular sieve	HZSM-5(23)	Because of its abundant acidity, molecular sieves can effectively promote the aromatic hydrocarbon structurization of oil shale during pyrolysis	30.93%	86
	Al-SBA-15		67.24%	102
Co-pyrolysis substrate	peanut shell: oil shale = 1:3	The interaction between peanut shells and oil shale during pyrolysis promotes the formation of aliphatic and aromatic hydrocarbons in the oil, reduces the average carbon chain length, and increases the content of light oil.	14.4%	103
	mushroom		53.97%	74
Composite catalysts	Co/MOF	Reduce the activation energy of oil shale pyrolysis and promote the cracking, aromatization and coking reactions of volatile matter.	44.90%	95
	20$CoCl_2·6H_2O$ 5MMT		46.81%	98

[a]Percentage of reduced activation energy = $(E_{OS} − E_{catalysts})/E_{OS} * 100\%$. E_{OS} is the activation energy required for the pyrolysis of oil shale without a catalyst, and $E_{catalysts}$ is the activation energy required for the pyrolysis of oil shale with catalysts.

olefins, guiding the conversion of kerogen to low-molecular-weight hydrocarbons.[29,61]

Therefore, the design of the catalyst should take the active sites of the catalyst into account, which have an important impact on the performance of the catalyst. At the same time, the physical and chemical adsorption between the catalyst and the substrate can adsorb organic substances in oil shale, prolong their residence time, promote further cracking reactions, and improve the generation rate and selectivity of the product. Therefore, the addition of catalysts is crucial for achieving efficient and highly selective in situ conversion of oil shale. By continuous optimization of the design and performance of catalysts, the efficiency and product quality of in situ pyrolysis of oil shale can be further improved, providing important support for sustainable energy development.

4. TYPES OF CATALYST

In practical applications, traditional in situ extraction of oil shale requires high energy consumption, and the thermal cracking products are prone to dehydrogenation reactions, generating a large amount of semi coke products. This results in few light fractions in oil shale oil and relatively poor product quality. Therefore, many researchers have begun to use in situ pyrolysis catalysts to solve this problem, hoping to effectively reduce the activation energy required for the pyrolysis reaction and improve the yield and quality of shale oil. At present, commonly used catalysts mainly include natural minerals, metals, metal oxides and salts, molecular sieves, copyrolysis substrates, and composite catalysts.

4.1. Natural Minerals. Natural minerals have large reserves and porous structures, low cost, are easy to obtain, and are rich in metal elements. Their catalytic performance is similar to that of zeolite. The commonly used natural mineral

catalysts are mainly montmorillonite, gypsum, kaolin, calcite, pyrite et al. These minerals are commonly present in oil shale.[29,62,63]

Al-Harahsheh et al.[64] conducted a relevant study on the influence of Jordanian oil shale minerals on its pyrolysis using Jordanian oil shale as raw material. They found that the presence of minerals could reduce the activation energy required for oil shale pyrolysis, thereby promoting the pyrolysis reaction. As shown in Figure 5, the study found that
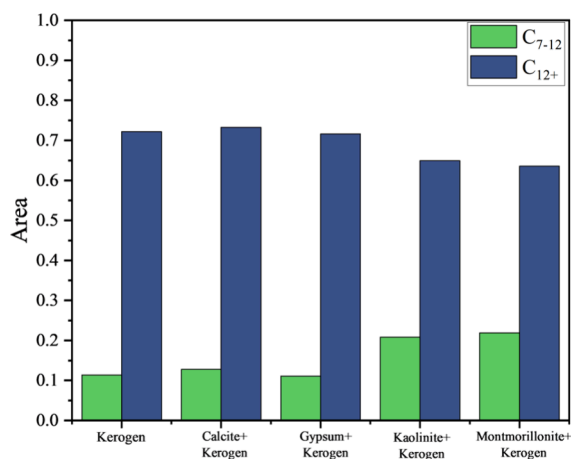

Figure 5. Carbon-number distribution of collected oil component from the pyrolysis of kerogen with and without different minerals.[29] Reprinted in part with permission from ref 29. Copyright 2014 American Chemical Society.

montmorillonite and kaolinite were clay catalysts with a large number of Lewis acid sites, which could trigger the cracking of alkanes and olefins, guide the conversion of kerogen to low molecular weight hydrocarbons, promote the generation of light oil products and reduce the production of residues and olefins.[29,61,65]

Compared to montmorillonite and kaolinite, gypsum is a natural ore mainly composed of $CaSO_4$ with a relatively single acid site and only containing Brønsted acid catalytic sites. Due to its unique pore structure and crystalline water, the coke content is reduced during pyrolysis, resulting in a decrease in the semicoke content in the product.[29,66] Calcite is a type of calcium carbonate mineral, and research has found that

carbonates exhibit a reverse catalytic effect on the pyrolysis and hydrocarbon generation of kerogen.[66,67] The chemical composition of pyrite is FeS_2, and it is a sulfide matrix belonging to the equiaxed crystal system. Li and Yan found that pyrite had a positive effect on the pyrolysis of oil shale, which could catalyze the decomposition of organic matter, reduce the temperature of liquid hydrocarbon generation, increase the proportion of isomeric alkanes, promote the increase of gas and liquid hydrocarbon production.[68−70]

Therefore, natural ores are economically advantageous and important in the in situ catalytic cracking of oil shale. Nature ores have become important catalysts in the catalytic cracking process of oil shale due to their porous catalytic structure, metallic elements, adsorption, thermal stability, richness and low cost.[29,61,65] The catalytic activity of minerals for the pyrolysis of kerogen is in the order as follows: calcite < kaolinite < gypsum < montmorillonite. Montmorillonite and gypsum are typical strong catalysts, and pyrite also has a positive effect on the pyrolysis of oil shale, while kaolinite is a weak catalyst and calcite is a typical inhibitor.[66]

4.2. Metals. Transition metal catalysts, such as Fe, Co, Mo and Ni, are primarily used in the in situ catalytic conversion of oil shale. These catalysts possess unique electronic structures and redox properties that can effectively promote the cracking of organic matter in oil shale.

In order to evaluate the impact of these metals on the pyrolysis of oil shale, Chaffee et al.[71] conducted relevant research (shown in Figure 6) and found that most of the organic matter in Jordanian oil shale were converted into asphaltene oil at 355 °C with a low yield, and almost all organic matter was converted into oil at 425 °C with the addition of catalysts such as Fe/Cu/Sn/NaAlO$_2$.

Chaffee et al.[72] also compared the differences in structural and activity of five Jordanian oil shales under Mo catalysis, pointing out that even oil shales deposited in the same region at the same time had significant differences. Jackson et al.[73] investigated the differences in the structure and activity of Cu/Fe/Ni/Co/Mo catalysts with and without low and high sulfur oil shale under N_2/H_2 atmospheres (as shown in Figure 7).

Therefore, in the in situ catalytic conversion process of oil shale, metal catalysts can effectively promote the cracking of organic matter in oil shale, thereby converting it to asphaltene oil at lower temperatures. When the temperature rises to 425 °C, almost all organic matter can be converted into oil,
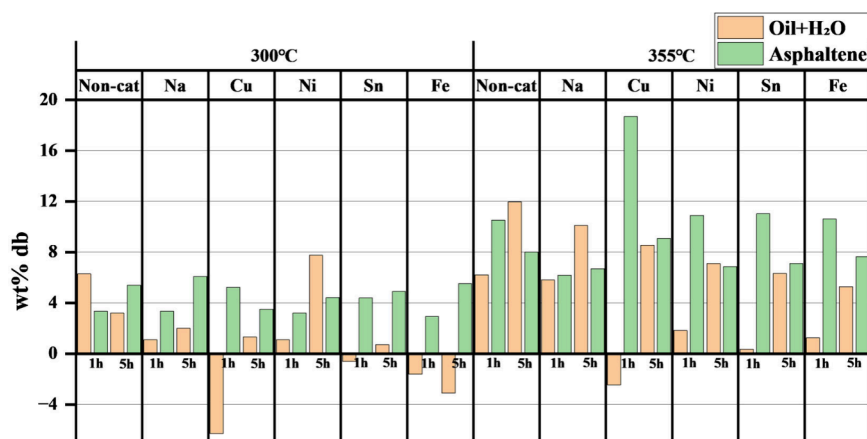

Figure 6. Effect of reaction time on the oil + H$_2$O and asphaltene yields of Jordanian oil shale reacted in CO with 1:1 water to oil shale ratio at 300 and 355 °C with different additives.[71] Reprinted in part with permission from ref 71. Copyright 2011 Elsevier Ltd.
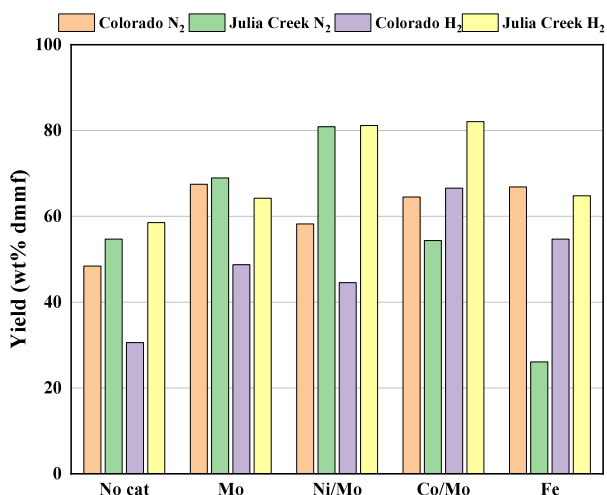
Figure 7. Effect of catalysts on CH_2Cl_2-solubles + hydrocarbon gas + sulfide gas + water yield.[73] Reprinted in part with permission from ref 73. Copyright 2014 Elsevier B.V.

especially Co and Ni, which can promote the conversion of organic matter in oil shale to higher-value aromatic hydrocarbons, improve the chemical composition and quality of pyrolysis oil, and significantly increase oil production.

4.3. Metal Oxides and Salts. Catalysts such as metal oxides, metal sulfides, and halides have abundant catalytic active sites and high stability and durability, which can accelerate reaction rates and selectivity and can be adapted to different needs and reaction conditions.

In order to investigate the impact of these catalysts on the in situ catalytic pyrolysis of oil shale, researchers have conducted extensive research. Li et al.[52] investigated the effects of transition metal salts ($CoCl_2·6H_2O/MnSO_4·H_2O$) and pyrolysis conditions on the yield and characteristics of Huadian oil shale products (presented in Figure 8). The maximum oil yield was 21.59 wt % at 520 °C. Cobalt salts, as active centers, accelerated the breaking of chemical bonds in organic matter and increased the content of aromatics in shale oil. The
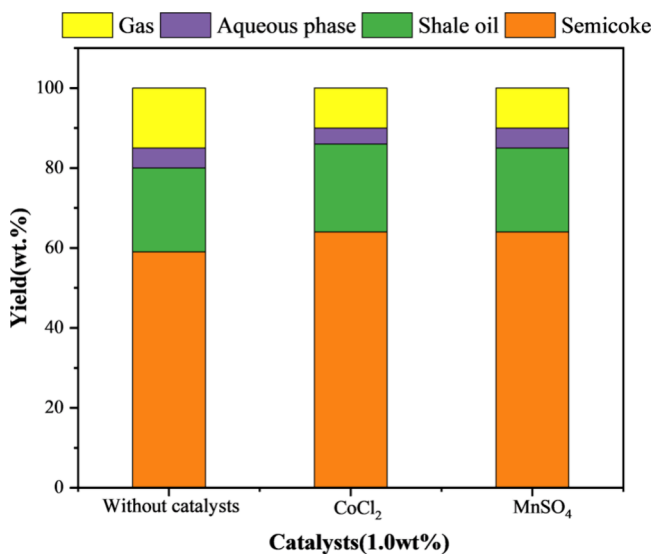

Figure 8. Average yields of products produced from the catalytic pyrolysis of oil shale.[52] Reprinted in part with permission from ref 52. Copyright 2015 Elsevier B.V.

production of acid indicated that manganese salts were not suitable as candidate catalysts. The research group also conducted a copyrolysis study of waste mushroom matrix and oil shale, and found that there was a good synergistic effect at 490−590 °C, which could promote the generation of oil and gas and reduce the solid residues.[74] Additionally, they investigated the mixed pyrolysis of waste mushroom matrix and oil shale semicoke for the preparation of bio-oil.[75]

Chu et al.[53] studied the catalytic cracking of Huadian oil shale by $FeCl_2·4H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$ and $ZnCl_2$. They found that the catalytic efficiency was highest for Ni salts, followed by Co, Zn and Fe salts, which could promote the aromatization of aliphatic hydrocarbons as presented in Figure 9. Pan et al.[76] investigated the impact of transition metal salts
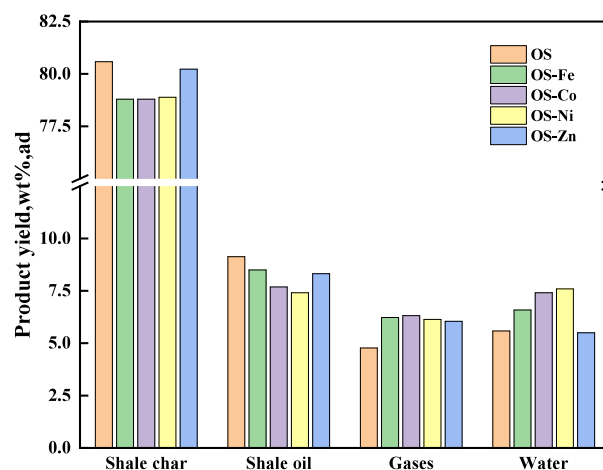

Figure 9. Effect of transition metal salts on the product yield of oil shale pyrolysis.[53] Reprinted in part with permission from ref 53. Copyright 2017 Estonian Academy Publishers.

such as Fe_2O_3, $CoCl_2·6H_2O$ and $MnSO_4·H_2O$ on the pyrolysis conditions and products of Jimsa oil shale. The results indicated that $CoCl_2·6H_2O$ had the best catalytic effect, yielding the highest amounts of CO, ethylene, and propylene with the cracking temperature dropping to 330~650 °C.

Wang et al.[77] investigated the different effects of Fe_2O_3 and $CaCO_3$ catalysts on the cracking gas of oil shale at 520 °C. As shown in Figure 10, different catalysts could lead to different changes in the physical structure of oil shale, resulting in different sacondary cracking reactions and the generation of different products. $CaCO_3$ promoted the generation of gas products, while Fe_2O_3 promoted the generation of liquid products. Wang et al.[78] studied oil shale produced in the Huadian and Fushun, and discovered that alkali metal carbonates such as K, Mg, Na and Ca, had different catalytic effects on oil shale. Among these, $MgCO_3$ demonstrated significant catalytic activity compared with other alkali metal carbonates. Wang et al. found that the conversion of kerogen to short chain ($C_6~C_{12}$) alkanes and olefins could be promoted by alkaline earth metal oxides.[79]

Metal oxides and halides could promote the pyrolysis of oil shale. $CoCl_2·6H_2O$ had the best effect. It significantly increased the content of aromatics in shale oil and promotes the generation of CO, ethylene and propylene in a lower temperature range (330~650 °C), and increased the production of light oil and helps to reduce the energy consumption required for pyrolysis. However, sulfides such as $MnSO_4·H_2O$, were not suitable as catalysts for oil shale
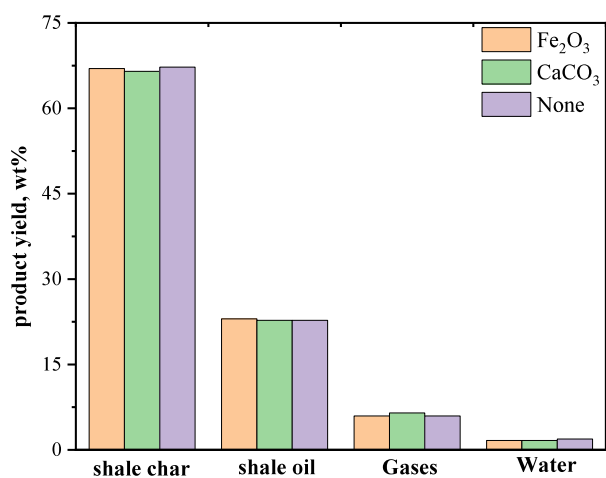
Figure 10. Influence of different catalysts on the yield of products derived by retorting Dachengzi oil shale.[77] Reprinted in part with permission from ref 77. Copyright 2018 Estonian Academy Publishers.

Figure 11. Carbon number distribution of *n*-alkanes and *n*-alkenes of shale oil samples.[85] Reprinted in part with permission from ref 85. Copyright 2020 Elsevier B.V.

pyrolysis. It might be due to their ability to produce acid substances during the reaction process, which had a negative impact on the quality of the oil.

4.4. Molecular Sieves. Molecular sieves are porous aluminosilicate materials with unique pore structure, tunable acidic sites and good hydrothermal stability.[80−82] They are widely used in the fields of petroleum, advanced chemical preparations, and catalysts.

Scholars have conducted extensive research and find that ZSM-5 zeolite catalyst can promote the conversion of oil shale in the Kark region of Pakistan into gas products and shale char, and promote the conversion of long-chain alkanes and olefins into low molecular weight and short-chain alkanes, but reduced the yield of shale oil.[83,84] To further investigate the influence of different Si/Al ratios, Chang et al. conducted a more in-depth study using Huadian oil shale as the raw material. The results, as shown in Figure 11, indicated that ZSM-5 (25) and ZSM-5 (38) could promote the inclusion of more aromatic hydrocarbons in shale oil, with content as high as 59.39% and 56.46%, respectively.[85]

Park et al.[86] examined the pyrolysis of acidic zeolite with black pine and Cookelst oil shale, and they discovered that different types of molecular sieves had distinct impacts on the catalytic pyrolysis of oil shale. Molecular sieves were found to be effective in reducing the activation energy required for the pyrolysis of oil shale, as well as lowering the maximum decomposition temperature of oil shale to around 420 °C.[86] The SO₃H-SBA-15 catalyst prepared by Meng et al., could reduce the activation energy down to 78 kJ/mol during the conversion process of oil shale pyrolysis.[87] Bozkurt et al.[88] investigated the synergistic pyrolysis effect of oil shale and LDPE at 600∼800 °C (shown in Figure 12), and found that the addition of terracotta, bentonite and molecular sieves could promote oil formation. Molecular sieves had the best catalytic performance due to their large specific surface area and acidic function.

In the in situ catalytic pyrolysis process of oil shale, molecular sieves could selectively adsorb and separate hydrocarbon compounds due to their highly ordered micropores and pore structures, prolonging their residence time and promoting further cracking. Meanwhile, molecular sieves with
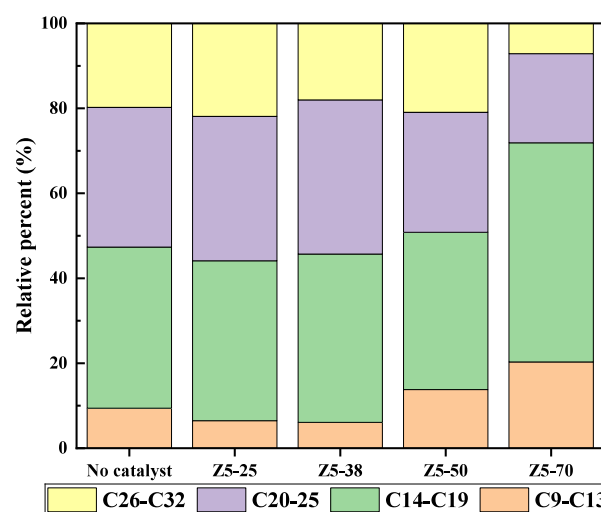
specific pore sizes and acidic sites provided the active sites and reaction surfaces required for the cracking reactions, accelerating the progress of cracking reactions. Although molecular sieve catalysts had many advantages in catalytic pyrolysis, such as high activity and selectivity, they also had the disadvantage of easy coking. Coking was caused by the deposition of carbon on the surface of the catalyst. As the reaction proceeds, carbon accumulated on the surface of the molecular sieve, leading to a gradual decrease or even deactivation of the catalyst. This would affect the lifespan and stability of the catalyst, reducing its effective usage time and increasing production costs.

4.5. Copyrolysis Substrates. In copyrolysis, the unique chemical structures and reactivity of various raw materials can promote each other and stimulate higher reaction activity during the pyrolysis process, thereby effectively improving the yield of products.

Yu et al.[89] reported the copyrolysis characteristics of oil shale and microalgae and a significant synergistic effect was achieved when the oil shale content was 3 wt % as depicted in Figure 13. Kartal et al.[90] investigated the effects of various process parameters on the liquefaction products of NİĞDE-ULUKI-ŞLA oil shale. MoO₃ had the highest efficiency of 9 wt % at 400 °C. At the same time, the yields of oil and gas production were significantly increased when using waste paper for cocracking. Chen et al.[91] proposed a model for the copyrolysis of oil shale and biomass, as shown in the Figure 14. The accuracy and rationality of the model were confirmed by comparing the predicted results to the experimental results of fixed-bed and thermogravimetric analysis.

Kruusement et al.[92] evaluated the noncatalytic liquefaction and Ni-catalytic gasification processes of spruce needles, rushes, peat and oil shale under supercritical water/Ar conditions using hydrothermal method. The results indicated that these solid fuels could be effectively converted into liquid and gaseous products with a higher energy density. Kim et al.[86] investigated the in situ catalytic copyrolysis process of Kukersite oil shale with Pinus nigra catalyzed by acidic zeolites such as HZSM-5 (23), HBeta(25) and HY(30). They found that HZSM-5 (23) could effectively catalyze the generation of
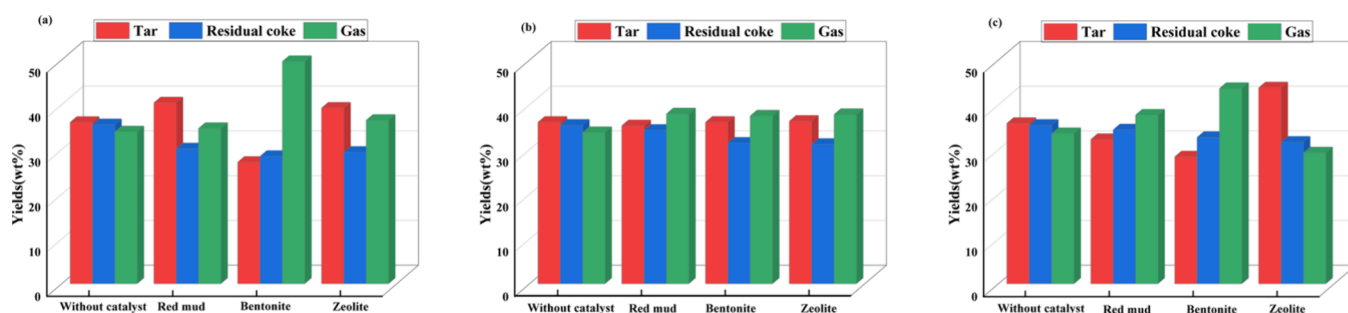
Figure 12. Effect of weight percentage of different catalyst on the yields, (a) 0.5 wt %, catalyst, (b) 2 wt %, catalyst, (c) 4 wt %, catalyst.[88] Reprinted in part with permission from ref 88. Copyright 2016 Elsevier Ltd.
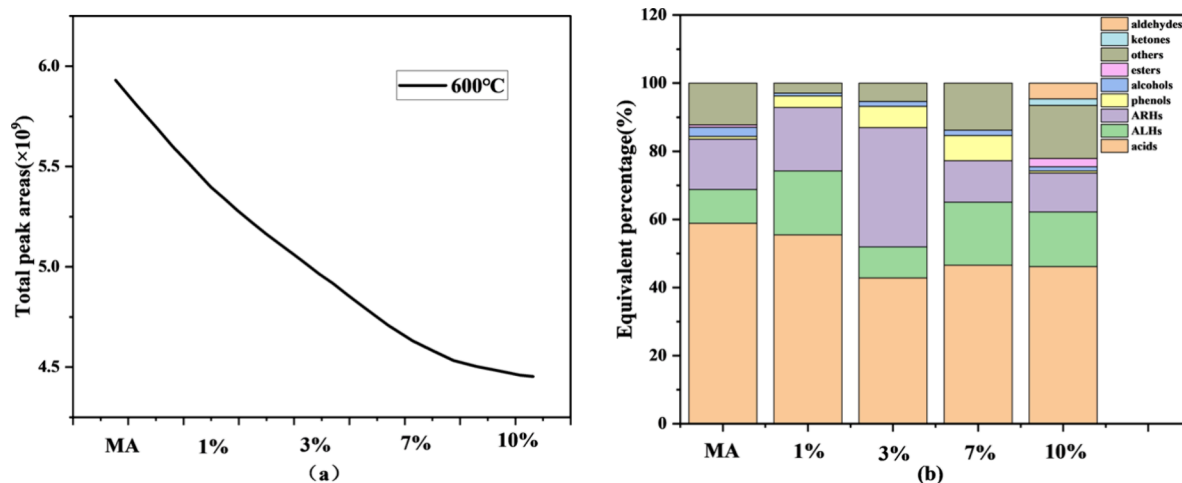

Figure 13. Effect of OS mass ratio at 600 °C: (a) Total peak areas of condensable products; (b) Products distribution.[89] Reprinted in part with permission from ref 89. Copyright 2018 Elsevier Ltd.
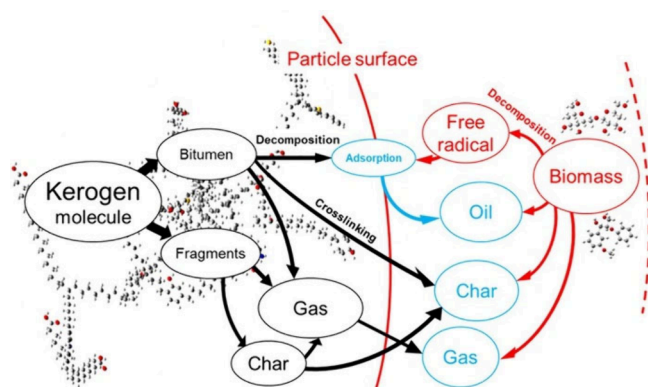

Figure 14. Model diagram of the copyrolysis.[91] Reprinted in part with permission from ref 91. Copyright 2021 Elsevier Ltd.

aromatics, and Pinus nigra had a certain synergistic effect on aromatics generation, as shown in Figure 15.

During the in situ catalytic pyrolysis of oil shale, due to the high ash content of oil shale, which is rich in various minerals such as calcite, pyrite, and montmorillonite, they can be used as a catalyst for copyrolysis substrates. The heat and gas generated by the copyrolysis substrates can provide the necessary energy for the pyrolysis of oil shale. The synergistic effects improve the overall performance of the catalyst and facilitate the pyrolysis process, which not only alleviate environmental pollution but also reduce energy consumption and has great application prospects.

4.6. Composite Catalysts. Composite catalysts are a new type of catalyst that load catalytically active components onto a carrier. The carrier can be composed of molecular sieves, alumina, shale ash, and other substances. The synergistic effect between each component can promote the pyrolysis of oil shale and improve the product quality.

Meng et al.[93] used natural clay-based catalysts to in situ modify oil shale, enhancing oil production and quality as depicted in Figure 16. The SO$_3$H-APG catalyst demonstrated a positive catalytic effect, which could be obtained by ball milling clay, augite and 3-mercapto propyltrimethoxysilane, followed by oxidation with H$_2$O$_2$. The yields of oil products reached 54.93% when the −SO$_3$H was 4 mmol/g.

Zhang et al.[94] studied the effect of HZSM-5 and HY molecular sieves, as well as their metal (Co, Mo, Fe) loaded composite catalysts on the yields of shale oil in N$_2$/H$_2$. The results indicated that the addition of catalysts significantly increased the content of low-carbon chain hydrocarbons in shale oil while reducing the content of long-chain hydrocarbons. Specifically, the addition of Fe/HY catalysts under nitrogen atmosphere showed the greatest change with the content of low-carbon chain hydrocarbons increasing by 83.43 wt % and the content of long-chain hydrocarbons decreasing by 98.52 wt %. Furthermore, the catalyst proved to be highly effective in eliminating nitrogen and sulfur compounds from shale oil, reducing the total amount of nitrogen and sulfur compounds to 55.00 wt %.

The nano Co/MOF and Ni/MOF prepared by Wang et al.[95] reduced the activation energy of oil shale pyrolysis reaction by
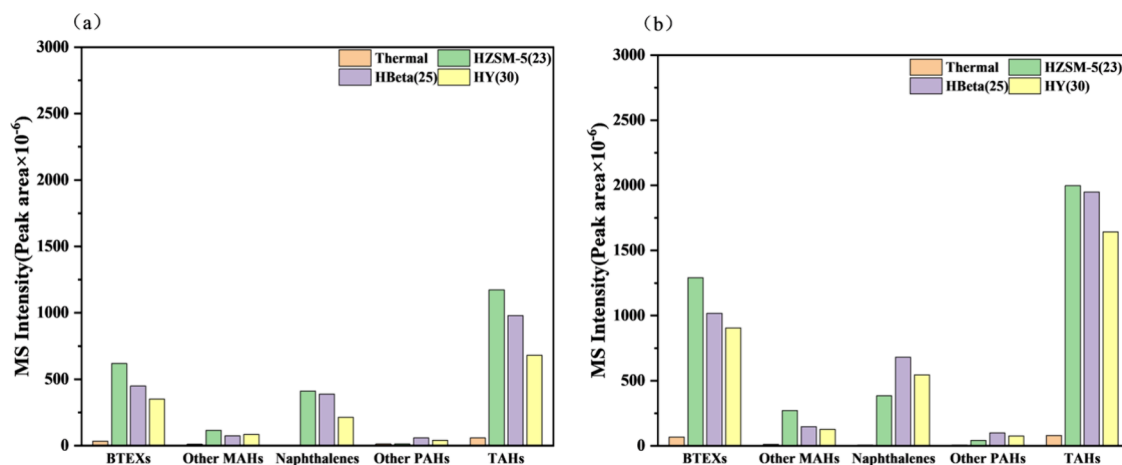
Figure 15. MS peak intensities of aromatic hydrocarbons obtained from the thermal and catalytic pyrolysis of (a) BPW and (b) KOS.[86] Reprinted in part with permission from ref 86. Copyright 2021 Elsevier B.V.
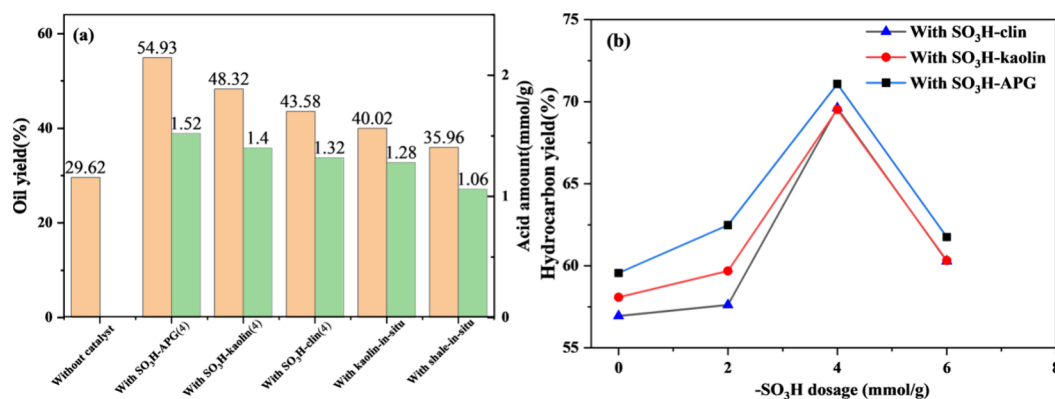

Figure 16. Influence of (a) acid amount and (b) − SO_3H dosage on the quality of shale oil.[93] Reprinted in part with permission from ref 93. Copyright 2021 Elsevier Ltd.

32 and 25 kJ/mol as depicted in Figure 17, respectively. With the addition of catalysts, there was an increase in the amount of aromatics, olefins, and alkanes in the products, while there was a decrease in the amount of oxygen-containing compounds. A novel Cu@zeolite nano in situ conversion catalyst synthesized
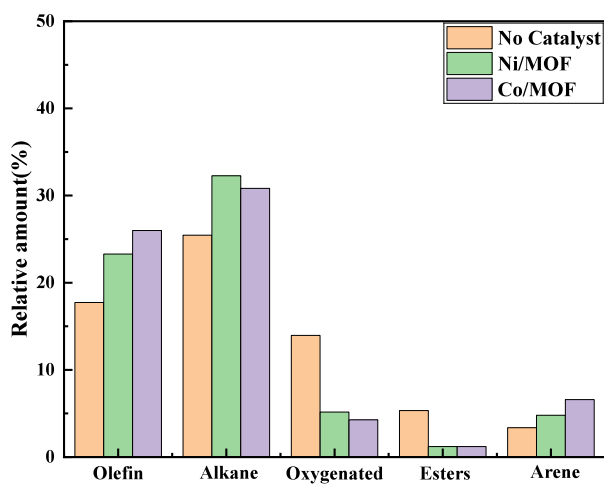

Figure 17. Effect of different catalysts on shale oil fraction.[95] Reprinted in part with permission from ref 95. Copyright 2023 Elsevier B.V.

by Jin et al.[60] was able to reduce the pyrolysis temperature of oil shale from 410 to 360 °C, and the activation energy required for pyrolysis was also reduced from 190.73 to 147.95 kJ/mol.

Li et al.[96] reported on W−Ni/γ-Al_2O_3 catalyst couples an aromatic hydrocarbon hydrogenation and a ring to enhance the conversion of shale oil into clean fuel. It was found that the tungsten-loaded alumina carrier had the most significant catalytic effect on hydrocarbon products. The load of tungsten directly affected the pore structure and acidity of the catalyst, which could be enhanced under a high tungsten loading. A kinetic model for hydrogenation desulfurisation, denitrogenation and cracking were also established.[97] Jiang et al. conducted in-depth reasearch on the catalytic activity of montmorillonite and $CoCl_2 \cdot 6H_2O$ catalysts with different mixing ratios in the thermal decomposition process of oil shale, and found that the mixed catalysts help to increase the generation of low molecular weight hydrocarbon products.[98]

Jia et al.[99] studied the effect of shale ash-loaded $ZnCl_2$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ catalysts on the pyrolysis of Fushun oil shale as depicted in Figure 18. It was found that shale ash could promote the cracking of oil shale, increase the content of short chain aliphatic hydrocarbons, and enhance aromatization reactions. The catalytic activity sequence was Cu > Ni > Zn. Pan et al.[100] also studied the catalytic effect of shale ash-loaded binary transition metal $CuCl_2 \cdot 2H_2O$ + $NiCl_2 \cdot 6H_2O$
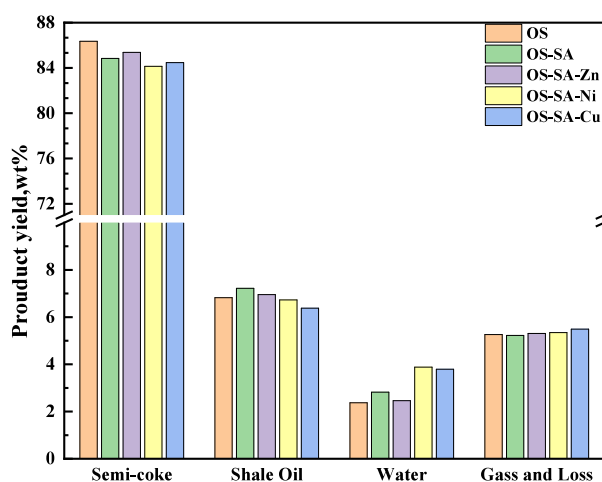
Figure 18. Effects of SA and its supported transition metal salts on the yield of OS pyrolysis products.[99] Reprinted in part with permission from ref [99]. Copyright 2019 MDPI.

catalysts and reviewed the recent progress of oil shale catalytic cracking.[101]

Therefore, composite catalysts retain the original catalytic properties of the carrier and synergistically act with the loaded active components to further promote the cracking of organic matter in oil shale into short-chain hydrocarbons while reducing the required activation energy and improving the quality of shale oil.

5. CONCLUSION AND OUTLOOK

This paper reviewed the reaction mechanism and catalyst design of oil shale pyrolysis and analyzed the effects of various catalysts on the yield and composition of pyrolysis products. It had been shown that clay-based catalysts utilized Lewis acid sites to promote the cracking of alkanes and olefins, converting them to low molecular weight hydrocarbons. Metal catalysts promoted the conversion of organic matter to asphaltene oil at lower temperatures. Metal oxides and halides, especially $CoCl_2 \cdot 6H_2O$, could effectively increase the content of aromatics in the product. Molecular sieves accelerated the cracking reaction with their ordered microporous structures and specific acidic sites. The interaction between oil shale and copyrolysis substrates could effectively promote the pyrolysis process of oil shale. Composite catalysts improved cracking efficiency through the synergistic effect of carrier and active components.

Although researchers have explored various catalysts with different characteristics and structures for in situ catalytic conversion of oil shale, the research on catalysts for the pyrolysis of oil shale is still in the laboratory stage at home and abroad. Challenges such as catalyst deactivation, regeneration difficulties, and economic benefits are inevitable faced in practical applications. In order to overcome these problems, it is necessary to deeply understand the mechanism of catalyst deactivation at the basic research level, explore new catalytic materials, and combine modern technologies such as microwave radiation, plasma technology, and catalytic pyrolysis to develop a feasible in situ catalyst injection process. These technologies may help to achieve faster heat transfer, higher reaction rates, and lower energy consumption.

Promoting this technology in the in situ catalytic conversion of oil shale can effectively improve oil shale recovery and reduce pollutants in the mining process. Therefore, this research will promote the development of in situ catalytic conversion technology in oil shale to be more efficient, environmentally friendly, and economically feasible.

■ AUTHOR INFORMATION

Corresponding Authors

Junwen Wu − *State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 102206, P.R. China; State Center for Research and Development of Oil Shale Exploitation, Beijing 102206, P.R. China*; Email: wujw.syky@sinopec.com

Weichu Yu − *School of Chemistry and Environmental Engineering, Yangtze University, Jingzhou, Hubei 434023, P.R. China;* ⊙ orcid.org/0000-0001-6551-1950; Email: yuweichu@126.com

Authors

Aibin Wu − *State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 102206, P.R. China; State Center for Research and Development of Oil Shale Exploitation, Beijing 102206, P.R. China; School of Chemistry and Environmental Engineering, Yangtze University, Jingzhou, Hubei 434023, P.R. China;* ⊙ orcid.org/0000-0001-6632-2326

Liu Chen − *School of Chemistry and Environmental Engineering, Yangtze University, Jingzhou, Hubei 434023, P.R. China*

Jianzheng Su − *State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 102206, P.R. China; State Center for Research and Development of Oil Shale Exploitation, Beijing 102206, P.R. China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c04724

Author Contributions

⊥A.W. and L.C. contributed equally to this article.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Zhang, J.; Ding, Y. M.; Du, W. Z.; Lu, K. H.; Sun, L. L. Study on pyrolysis kinetics and reaction mechanism of beizao oil shale. *Fuel* **2021**, *296*, 120696.

(2) Al-Harahsheh, A.; Al-Ayed, O.; Al-Harahsheh, M.; Abu-El-Halawah, R. Heating rate effect on fractional yield and composition of oil retorted from el-lajjun oil shale. *J. Anal. Appl. Pyrolysis* **2010**, *89* (2), 239−243.

(3) Tong, X. G. Genesis and distribution of unconventional oil. *Acta Petrolei Sinica* **2012**, *33*, 20−26.

(4) Wang, Q.; Bai, J. R.; Sun, B. Z.; Guan, X. H.; Qin, H.; Li, S. H.; Sun, J. Integrated technology for oil shale exploitation. *J. Changchun Univ. Techonol. (Natural Science Edition)* **2007**, *28*, 54−58.

(5) Liu, Z. J.; Dong, Q. S.; Ye, S. Q.; Zhu, J. W.; Guo, W.; Li, D. C.; Liu, R.; Zhang, H. L.; Du, J. F. The situation of oil shale resources in china. *J. Jilin Univ. (Earth Science Edition)* **2006**, *36* (06), 869−876.

(6) Mulchandani, H.; Brandt, A. R. Oil shale as an energy resource in a CO₂ constrained world: the concept of electricity production with in situ carbon capture. *Energy Fuels* **2011**, *25* (4), 1633−1641.

(7) World Energy Council. *2010 survey of energy resources*; World Energy Council: London, UK, 2010.

(8) World Energy Council. *World energy resources 2016*; World Energy Council: London, UK, 2016.

(9) Qian, J. L.; Ying, L. *Oil shale: petroleum alternative*; China Petrochemical Press: Beijing, 2008.

(10) Guan, X.; Li, D. D.; Han, D. Y.; Zhu, T.; Cao, C. Y.; Feng, C. C.; Zhang, G. S.; Cao, Z. B. Development and utilization progress of foreign oil shale resources. *Contemporary Chem. Indus.* **2015**, *44* (01), 80−82.

(11) Ma, L.; Ying, X. Y.; Sun, H.; Fu, B. S. Present status of oil shale resource utilization in the world and its development prospects. *Global Geology* **2012**, *31* (04), 772−777.

(12) Zhao, W. Z.; Hu, S. Y.; Hou, L. H.; Yang, T.; Li, X.; Guo, B. C.; Yang, Z. Types and resource potential of continental shale oil in China and its boundary with tight oil. *Petrol. Explor. Develop.* **2020**, *47* (1), 1−11.

(13) Song, Y.; Li, Z.; Jiang, Z.; Luo, Q.; Liu, D.; Gao, Z. Progress and development trend of unconventional oil and gas geological research. *Petrol. Explor. Develop.* **2017**, *44* (4), 675−685.

(14) Zhang, D.; Ranjith, P. G.; Perera, M. S. A. The brittleness indices used in rock mechanics and their application in shale hydraulic fracturing: a review. *J. Petrol. Sci. Engineer.* **2016**, *143*, 158−170.

(15) Zou, C. N.; Zhang, G. Y.; Tao, S. Z.; Hu, S. Y.; Li, X. D.; Li, J. Z.; Dong, D. Z.; Zhu, R. K.; Yuan, X. J.; Hou, L. H.; et al. Geological features, major discoveries and unconventional petroleum geology in the global petroleum exploration. *Petrol. Explor. Develop.* **2010**, *37* (2), 129−145.

(16) Han, X. X.; Jiang, X. M.; Cui, Z. G. Studies of the effect of retorting factors on the yield of shale oil for a new comprehensive utilization technology of oil shale. *Appl. Energy* **2009**, *86* (11), 2381−2385.

(17) Wang, S.; Jiang, X.; Han, X.; Tong, J. Investigation of chinese oil shale resources comprehensive utilization performance. *Energy* **2012**, *42*, 224−232.

(18) Altun, N. E.; Hicyilmaz, C.; Hwang, J. Y.; Suat Bagci, A.; Kok, M. V. Oil shales in the world and turkey: reserves, current situation and future prospects: a review. *Oil Shale* **2006**, *23*, 211−227.

(19) Crawford, P.; Biglarbigi, K.; Dammer, A.; Knaus, E. Advances in world oil-shale production technologies. *SPE annual technical conference and exhibition: society of petroleum engineers*. Denver, CO, Sept. 21-24, 2008, SPE-116570-MS. DOI: 10.2118/116570-MS

(20) Knyazeva, A. G.; Maslov, A. L.; Martemyanov, S. M. A two-phase model of shale pyrolysis. *Fuel* **2018**, *228*, 132−139.

(21) Raukas, A.; Punning, J. Environmental problems in the estonian oil shale industry. *Energy & Environm. Sci.* **2009**, *2*, 723−728.

(22) Jiang, X.; Han, X.; Cui, Z. New technology for the comprehensive utilization of chinese oil shale resources. *Energy* **2007**, *32*, 772−777.

(23) Brandt, A. R. Converting oil shale to liquid fuels: energy inputs and greenhouse gas emissions of the shell in situ conversion process. *Environm. Sci. Technol.* **2008**, *42*, 7489−7495.

(24) Liu, D. X.; Wang, H. Y.; Zheng, D. W.; Fang, C. H.; Ge, Z. X. World progress of oil shale in-situ exploitation methods. *Natural gas industry* **2009**, *29*, 128−132.

(25) Soeder, D. J. The successful development of gas and oil resources from shales in north america. *J. Petrol. Sci. Engineer.* **2018**, *163*, 399−420.

(26) Pan, Y.; Peng, J.; Yang, S. C.; Fu, J. W.; Li, L. Review of electric heating technology of oil shale and its simulation. *J. Anal. Appl. Pyrolysis* **2023**, *175*, 106205.

(27) Saif, T.; Lin, Q.; Bijeljic, B.; Blunt, M. J. Microstructural imaging and characterization of oil shale before and after pyrolysis. *Fuel* **2017**, *197*, 562−574.

(28) Deng, S.; Wang, Z.; Gu, Q.; Meng, F.; Li, J.; Wang, H. Extracting hydrocarbons from huadian oil shale by sub-critical water. *Fuel Process. Technol.* **2011**, *92* (5), 1062−1067.

(29) Hu, M.; Cheng, Z.; Zhang, M.; Liu, M.; Song, L.; Zhang, Y.; Li, J. Effect of calcite, kaolinite, gypsum, and montmorillonite on huadian oil shale kerogen pyrolysis. *Energy Fuels* **2014**, *28* (3), 1860−1867.

(30) Amer, M. W.; Alhesan, J. S. A.; Marshall, M.; Fei, Y.; Jackson, W. R.; Chaffee, A. L. Energy efficient method of supercritical extraction of oil from oil shale. *Energy Conver. Manag.* **2022**, *252*, 115108−115118.

(31) Kang, S.; Sun, Y.; Deng, S.; Li, S.; Su, Y.; Guo, W.; Li, J. Extraction of huadian oil shale in subcritical FeCl₂ solution. *Fuel Process. Technol.* **2021**, *211*, 106571−106579.

(32) Kang, S.; Sun, Y.; Qiao, M.; Li, S.; Deng, S.; Guo, W.; Li, J.; He, W. The enhancement on oil shale extraction of FeCl₃ catalyst in subcritical water. *Energy* **2022**, *238*, 121763−121770.

(33) Liang, X.; Zhao, Q.; Dong, Y.; Guo, L.; Jin, Z.; Liu, Q. Experimental investigation on supercritical water gasification of organic-rich shale with low maturity for syngas production. *Energy Fuels* **2021**, *35*, 7657−7665.

(34) Hillier, J. L.; Fletcher, T. H. Pyrolysis kinetics of a green river oil shale using a pressurized TGA. *Energy Fuels* **2011**, *25* (1), 232−239.

(35) Park, D. K.; Song, E. Pyrolysis and char oxidation characteristics of oil shales and coal in a thermogravimetric analyzer. *Canad. J. Chem. Engineer.* **2017**, *95* (12), 2367−2373.

(36) Zhang, Z.; Zhang, H.; Chai, J.; Zhao, L.; Zhuang, L. Reactive molecular dynamics simulation of oil shale combustion using the ReaxFF reactive force field. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2021**, *43*, 349−360.

(37) Skala, D.; Kopsch, H.; Sokic, M.; Neumann, H.; Jovanovic, J. Thermogravimetrically and differential scanning calorimetrically derived kinetics of oil shale pyrolysis. *Fuel* **1987**, *66* (9), 1185−1191.

(38) Ru, X.; Cheng, Z.; Song, L.; Wang, H.; Li, J. Experimental and computational studies on the average molecular structure of chinese huadian oil shale kerogen. *J. Mol. Struct.* **2012**, *1030*, 10−18.

(39) Braun, R. L.; Rothman, A. J. Oil-shale pyrolysis: kinetics and mechanism of oil production. *Fuel* **1975**, *54* (2), 129−131.

(40) Jaber, J. O.; Probert, S. D. Pyrolysis and gasification kinetics of jordanian oil-shales. *Applied Energy* **1999**, *63* (4), 269−286.

(41) Ribas, L.; Neto, J. M. R.; França, A. B.; Alegre, H. K. P. The behavior of irati oil shale before and after the pyrolysis process. *J. Petrol. Sci. Engineer.* **2017**, *152*, 156−164.

(42) Kang, Z.; Zhao, Y.; Yang, D. Review of oil shale in-situ conversion technology. *Appl. Energy* **2020**, *269*, 115121.

(43) Lai, D.; Zhan, J. H.; Tian, Y.; Gao, S.; Xu, G. Mechanism of kerogen pyrolysis in terms of chemical structure transformation. *Fuel* **2017**, *199*, 504−511.

(44) Xiong, Y.; Zhang, L.; Chen, Y.; Wang, X.; Li, Y.; Wei, M.; Jiang, W.; Lei, R. The origin and evolution of thermogenic gases in organic-rich marine shales. *J. Petrol. Sci. Engineer.* **2016**, *143*, 8−13.

(45) Zhao, K. A.; Sun, P. C.; Yu, F. G.; Liu, R.; Zhang, D. Y. Study on reservoir physical properties of oil shale during heating in minhe basin. *Xinjiang Petrol. Geology* **2020**, *41* (02), 158−163.

(46) Liu, Y.; Liu, S. M.; Zhang, R.; Zhang, Y. The molecular model of Marcellus shale kerogen: Experimental characterization and structure reconstruction. *Internat. J. Coal Geol.* **2021**, *246*, 103833.

(47) Shi, K. Y.; Chen, J. Q.; Pang, X. G.; Jiang, F. J.; Hui, S. S.; Zhang, S. J.; Pang, H.; Wang, Y. Y.; Chen, D.; Yang, X. B.; Li, B. Y.; Pu, T. Y. Average molecular structure model of shale kerogen: experimental characterization, structural reconstruction, and pyrolysis analysis. *Fuel* **2024**, *355*, 129474.

(48) Qing, W.; Xinmin, W.; Shuo, P. Study on the structure, pyrolysis kinetics, gas release, reaction mechanism, and pathways of Fushun oil shale and kerogen. *Fuel Process. Technol.* **2022**, *225*, 107058.

(49) You, Y. L.; Wang, X. Y.; Han, X. X.; Jiang, X. M. Kerogen pyrolysis model based on its chemical structure for predicting product evolution in China. *Fuel* **2019**, *246* (15), 149−159.

(50) Zhang, C.; Yao, Y. B.; Elsworth, D.; Liu, D. X.; Ju, Y. W.; Dong, Y. G.; Ye, S. Microstructure characterization of kerogen in mature shale: molecular investigation of micropore development. *J. Natur. Gas Sci. Engineer.* **2021**, *95*, 104239.

(51) Zhang, H. Y.; Ahmed, M.; Zhan, J. H. Recent advances in molecular simulation of oil shale kerogen. *Fuel* **2022**, *316*, 123392.

(52) Jiang, H.; Song, L.; Cheng, Z.; Chen, J.; Zhang, L.; Zhang, M.; Hu, M.; Li, J.; Li, J. Influence of pyrolysis condition and transition metal salt on the product yield and characterization via huadian oil shale pyrolysis. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 230−263.

(53) Chang, Z.; Chu, M.; Zhang, C.; Bai, S.; Ma, L. Investigation of the effect of selected transition metal salts on the pyrolysis of huadian oil shale, china. *Oil Shale* **2017**, *34* (4), 354−367.

(54) Gao, F. C.; Huang, J.; Ruan, Y.; Li, H.; Gong, P. Y.; Wang, F. L.; Tang, Q. W.; Jiang, Y. Y. Unraveling the structure transition and peroxidase mimic activity of copper sites over atomically dispersed copper-doped carbonized polymer dots. *Angew. Chem., Int. Ed.* **2023**, *62* (7), e202214042.

(55) Tang, Y. X.; Zhao, T. T.; Han, H. C.; Yang, Z. G.; Liu, J. R.; Wen, X. D.; Wang, F. L. Ir-CoO active centers supported on porous Al₂O₃ nanosheets as efficient and durable photo-thermal catalysts for CO₂ conversion. *Adv. Sci.* **2023**, *10* (15), 202300122.

(56) Yang, Z. Y.; Zhao, T. T.; Hao, S. Y.; Wang, R. T.; Zhu, C. Y.; Tang, Y. X.; Guo, C.; Liu, J. R.; Wen, X. D.; Wang, F. L. Large-scale synthesis of multifunctional single-phase Co₂C nanomaterials. *Adv. Sci.* **2023**, *10* (19), 202301073.

(57) Yang, Z. Y.; Zhao, T. T.; Tang, Y. X.; Jiang, Y. Y.; Kitagawa, H.; Wen, X. D.; Wang, F. L. Size-modulated photo-thermal catalytic CO₂ hydrogenation performances over Pd nanoparticles. *J. Catal.* **2023**, *424*, 22−28.

(58) Guo, C.; Tang, Y. X.; Yang, Z. Y.; Zhao, T. T.; Liu, J. R.; Zhao, Y. F.; Wang, F. L. Reinforcing the efficiency of photothermal catalytic CO₂ methanation through integration of Ru nanoparticles with photothermal MnCo₂O₄ nanosheets. *ACS Nano* **2023**, *17* (23), 23761−23771.

(59) Tang, Y. X.; Wang, H.; Guo, C.; Yang, Z. Y.; Zhao, T. T.; Liu, J. R.; Jiang, Y. Y.; Wang, W. L.; Zhang, Q.; Wu, D. S.; Zhao, Y. F.; Wen, X. D.; Wang, F. L. Ruthenium-Cobalt solid-solution alloy nanoparticles for enhanced photopromoted thermocatalytic CO₂ hydrogenation to methane. *ACS Nano* **2024**, *18* (17), 11449−11461.

(60) Jin, J. F.; Sun, J. S.; Lv, K. H.; Hou, Q. L.; Guo, X.; Liu, K. S.; Deng, Y.; Song, L. D. Catalytic pyrolysis of oil shale using tailored Cu@zeolite catalyst and molecular dynamic simulation. *Energy* **2023**, *278*, 127858.

(61) Wang, Q.; Zhang, H. X.; Chi, M. S.; Cui, D.; Xu, X. C. Effect of smectite on the pyrolysis of kerogen isolated from oil shale. *Chem. Indus. Engineer. Progress* **2016**, *35* (03), 766−772.

(62) Xinmin, W.; Qing, W.; Chunlei, W. Study of the effect of in situ minerals on the pyrolysis of oil shale in fushun, china. *RSC Adv.* **2022**, *12*, 20239−20250.

(63) Thiéry, V.; Bourdot, A.; Bulteel, D. Characterization of raw and burnt oil shale from dotternhausen: petrographical and mineralogical evolution with temperature. *Mater. Character.* **2015**, *106*, 442−451.

(64) Al-Harahsheh, M.; Al-Ayed, O.; Robinson, J.; Kingman, S.; Al-Harahsheh, A.; Tarawneh, K.; Saeid, A.; Barranco, R. Effect of demineralization and heating rate on the pyrolysis kinetics of jordanian oil shales. *Fuel Process. Technol.* **2011**, *92* (9), 1805−1811.

(65) Li, S. Y.; Lin, S. J.; Guo, S. H.; Liu, L. F. Catalytic effects of minerals on hydrocarbon generation in kerogen degradation. *J. Univ. Petrol.* **2002**, *01*, 69−71.

(66) Zhao, G. Y.; Liu, L. F.; Li, S. Y. Study on characteristics and kinetics of catalytic degradation from estonia kerogen. *Acta Sedimentologica Sinica* **2004**, *03*, 525−528.

(67) Corredor, E. C.; Deo, M. D. Effect of vapor liquid equilibrium on product quality and yield in oil shale pyrolysis. *Fuel* **2018**, *234*, 1498−1506.

(68) Gai, R.; Jin, L.; Zhang, J.; Wang, J.; Hu, H. Effect of inherent and additional pyrite on the pyrolysis behavior of oil shale. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 342−347.

(69) Yan, J.; Jiang, X.; Han, X.; Liu, J. A TG−FTIR investigation to the catalytic effect of mineral matrix in oil shale on the pyrolysis and combustion of kerogen. *Fuel* **2013**, *104*, 307−317.

(70) Li, K.; Zhao, Z.; Lu, H.; Liu, X.; Peng, P.; Hsu, C. S. Effects of inherent pyrite on hydrocarbon generation by thermal pyrolysis: an example of low maturity type-II kerogen from alum shale formation, sweden. *Fuel* **2022**, *312*, 122865.

(71) Fei, Y.; Marshall, M.; Jackson, W. R.; Gorbaty, M. L.; Amer, M. W.; Cassidy, P. J.; Chaffee, A. L. Evaluation of several methods of extraction of oil from a jordanian oil shale. *Fuel* **2012**, *92*, 281−287.

(72) Amer, M. W.; Marshall, M.; Fei, Y.; Jackson, W. R.; Gorbaty, M. L.; Cassidy, P. J.; Chaffee, A. L. A comparison of the structure and reactivity of five jordanian oil shales from different locations. *Fuel* **2014**, *119*, 313−322.

(73) Amer, M. W.; Marshall, M.; Fei, Y.; Roy Jackson, W.; Gorbaty, M. L.; Cassidy, P. J.; Chaffee, A. L. The structure and reactivity of a low-sulfur lacustrine oil shale compared with those of a high-sulfur marine oil shale. *Fuel Process. Technol.* **2015**, *135*, 91−98.

(74) Jiang, H.; Deng, S.; Chen, J.; Zhang, L.; Zhang, M.; Li, J.; Li, S.; Li, J. Preliminary study on copyrolysis of spent mushroom substrate as biomass and huadian oil shale. *Energy Fuels* **2016**, *30*, 6342−6349.

(75) Jiang, H.; Zhang, M.; Chen, J.; Li, S.; Shao, Y.; Yang, J.; Li, J. Characteristics of bio-oil produced by the pyrolysis of mixed oil shale semi-coke and spent mushroom substrate. *Fuel* **2017**, *200*, 218−224.

(76) Pan, N.; Yue, Y.; He, Z.; Lv, W. Influence of transition metal salts and pyrolysis conditions on the product yield via jimsar oil shale pyrolysis. *Oil Shale* **2020**, *37* (4), 304−318.

(77) Wang, S.; Song, L.; Jiang, X. Catalytic effects of Fe-and Ca-based additives on gas evolution during pyrolysis of dachengzi oil shale of China. *Oil Shale* **2018**, *35* (1), 39−55.

(78) Wang, Q.; Wu, H.; Jia, C. X.; Sui, Y. Effects of different alkali carbonates on oil shale pyrolysis. *Chem. Engineer. Machinery* **2015**, *42* (03), 333−340.

(79) Wang, Z.; Shi, W.; Song, W.; Li, S. Effects of metal oxides on yields and compositions of products from pyrolysis of oil shale. *J. Chem. Indus. Technol.* **2017**, *68* (10), 3884−3891.

(80) Tarach, K. A.; Martinez-Triguero, J.; Rey, F.; Gora-Marek, K. Hydrothermal stability and catalytic performance of desilicated highly siliceous zeolites ZSM-5. *J. Catal.* **2016**, *339*, 256−269.

(81) Wei, Z.; Xia, T.; Liu, M.; Cao, Q.; Xu, Y.; Zhu, K.; Zhu, X. Alkaline modification of ZSM-5 catalysts for methanol aromatization: the effect of the alkaline concentration. *Frontiers of Chem. Sci. Engineer.* **2015**, *9* (4), 450−460.

(82) Chen, H.; Wang, Y.; Sun, C.; Wang, X.; Wang, C. Synthesis of hierarchical ZSM-5 zeolites with CTAB-containing seed silicalite-1 and its catalytic performance in methanol to propylene. *Catal. Commun.* **2018**, *112*, 10−14.

(83) Williams, P. T.; Chishti, H. M. Influence of residence time and catalyst regeneration on the pyrolysis−zeolite catalysis of oil shale. *J. Anal. Appl. Pyrolysis* **2001**, *60* (2), 187−203.

(84) Williams, P. T.; Ahmad, N. Influence of process conditions on the pyrolysis of pakistani oil shales. *Fuel* **1999**, *78* (6), 653−662.

(85) Chang, Z.; Qu, Y.; Gu, Z.; Zhou, L.; Li, R.; Sun, Z.; Xu, M.; Chu, M. Production of aromatic hydrocarbons from catalytic pyrolysis of huadian oil shale using ZSM-5 zeolites as catalyst. *J. Anal. Appl. Pyrolysis* **2021**, *159*, 104990.

(86) Park, Y. K.; Siddiqui, M. Z.; Karagöz, S.; Han, T. U.; Watanabe, A.; Kim, Y. M. In-situ catalytic co-pyrolysis of kukersite oil shale with black pine wood over acid zeolites. *J. Anal. Appl. Pyrolysis* **2021**, *155*, 105050−105057.

(87) Meng, X. L.; Qi, Z.; Yu, C.; Bian, J.; Ma, Z.; Long, Q.; Su, J. Solid-acid catalytic conversion of oil shale: effects of sulfonicacid grafting on oil yield enhancing and quality improvement. *ACS Omega* **2021**, *6*, 5836−5845.

(88) Bozkurt, P. A.; Tosun, O.; Canel, M. The synergistic effect of co-pyrolysis of oil shale and low density polyethylene mixtures and

characterization of pyrolysis liquid. *J. Energy Instit.* **2017**, *90* (3), 355−362.

(89) Yu, Z.; Dai, M.; Huang, M.; Fang, S.; Xu, J.; Lin, Y.; Ma, X. Catalytic characteristics of the fast pyrolysis of microalgae over oil shale: analytical Py-GC/MS study. *Renewable Energy* **2018**, *125*, 465−471.

(90) Kartal, O. E.; Akin, S.; HasÇAkir, B.; Karaca, H. Liquefaction of oil shale: the effects of process parameters on the conversion of liquefaction products. *Oil Shale* **2017**, *34* (4), 336−353.

(91) Chen, B.; Yuan, M.; You, Y.; Wang, S.; Shen, J.; Han, X.; Jiang, X.; Guo, Y. Simulation analysis of co-pyrolysis of oil shale and wheat straw based on the combination of chain reaction kinetics and improved CPD models. *Energy Conver. Manag.* **2021**, *243*, 114405.

(92) Kruusement, K.; Luik, H.; Waldner, M.; Vogel, F.; Luik, L. Gasification and liquefaction of solid fuels by hydrothermal conversion methods. *J. Anal. Appl. Pyrolysis* **2014**, *108*, 265−273.

(93) Song, R.; Meng, X.; Yu, C.; Bian, J.; Su, J. Oil shale in-situ upgrading with natural clay-based catalysts: enhancement of oil yield and quality. *Fuel* **2022**, *314*, 123076−123084.

(94) Zhang, D. F. Study on pyrolysis and catalytic pyrolysis of liushuhe oil shale. *Dalian Univ. Technol.* **2012**.

(95) Wang, L.; Guo, J.-X.; Zhang, X.-J.; Gao, C.-H.; Xiong, R.-Y.; Kiyingi, W.; Luo, D. Nanoscale MOF-catalyzed pyrolysis of oil shale and kinetic analysis. *J. Anal. Appl. Pyrolysis* **2023**, *174*, 106149.

(96) Wang, H.; Dai, F.; Li, Z.; Li, C. Upgrading shale oil distillation to clean fuel by coupled hydrogenation and ring opening reaction of aromatics on W−Ni/γ-Al$_2$O$_3$ catalysts. *Energy Fuels* **2015**, *29*, 4902−4910.

(97) Dai, F.; Wang, H.; Gong, M.; Li, C.; Muhammad, Y.; Li, Z. Modeling of kinetic-based catalyst grading for upgrading shale oil hydrogenation. *Fuel* **2016**, *166*, 19−23.

(98) Jiang, H.; Hong, W.; Zhang, Y.; Deng, S.; Chen, J.; Yang, C.; Ding, H. Behavior, kinetic and product characteristics of the pyrolysis of oil shale catalyzed by cobalt-montmorillonite catalyst. *Fuel* **2020**, *269*, 117468−117477.

(99) Lu, H.; Jia, F.; Guo, C.; Pan, H.; Long, X.; Liu, G. Effect of shale ash-based catalyst on the pyrolysis of fushun oil shale. *Catalysts* **2019**, *9*, 900−914.

(100) Liu, X.; Pan, H.; Guo, C.; Di, X.; Hu, H. Effect of double transition metal salt catalyst on fushun oil shale pyrolysis. *Scanning* **2020**, *2020*, 6685299.

(101) Li, D.; Pan, H.; Di, X.; Liu, X.; Hu, H. Progress in catalytic pyrolysis of oil shale. *Scanning* **2021**, *2021*, 6759176.

(102) Fan, Y. S.; Han, Y.; Zhu, J. J.; Chen, Y. W.; Cai, Y. X.; Zhao, W. D. Production optimization of refined bio-oil through plasma coupling catalysis and composite zeolite effect of Al-SBA-15/HZSM-5. *Fuel* **2023**, *347*, 128494.

(103) Cui, S.; Yang, T. H.; Zhai, Y. M.; Zhu, Y. M.; Yu, Z. Q.; Kai, X. P. Investigation on the characteristics and interaction of co-pyrolysis of oil shale and peanut shell. *Fuel* **2023**, *340*, 127502.