Influence of transition metal salts and pyrolysis conditions on the product yield via Jimsar oil shale pyrolysis

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Abstract. *In this study, transition metal salts Fe_2O_3, $CoCl_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ were chosen to be catalysts for Jimsar oil shale pyrolysis. The pyrolysis behaviors of samples in the presence of different catalysts were compared using a thermogravometric (TG) analyzer first. Then the most effective catalytic pyrolysis process was analyzed by thermogravimetry-mass spectrometry (TG-MS). Of the three catalysts investigated, $CoCl_2 \cdot 6H_2O$ performed best. With $CoCl_2 \cdot 6H_2O$, the initial reaction temperature of the pyrolysis process was reduced by about 100 °C and the temperature range was decreased from 435–1000 °C to 330–650 °C. The yields of the pyrolysis products CO/ethene and propyne were the highest, while ethene accounted for the major part of CO/ethene. With increasing heating rate, the yields of alkenes and alkynes increased, those of H_2O, methane, alkanes and aromatic hydrocarbons decreased, whereas the yields of CO/ethene, H_2S, ethane, propene and CO_2/propane changed but a little. These results and analysis allowed a conclusion to be made that with $CoCl_2 \cdot 6H_2O$ as a catalyst, the most optimal heating rate for Jimsar oil shale pyrolysis was 5 °C/min.*

Keywords: *Jimsar oil shale, pyrolysis, transition metal, catalytic performance.*

1. Introduction

With the shortage of conventional energy resources and the continuous increase of demand for oil, oil shale is considered as an alternative energy resource for its abundant reserves. Usually, oil and gas can be obtained from oil shale by pyrolysis. The process of oil shale pyrolysis is influenced by factors such as heating rate, temperature, oil shale composition and content of ash, catalysts, etc. Catalysts can increase the rate of reaction and the production rate of volatiles, reduce energy consumption and improve the products quality [1–8]. Jiang et al. [9] studied the influence of pyrolysis conditions and transition metal salts on the yield and characteristics of products on an example of Huadian

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oil shale pyrolysis. The researchers demonstrated that $CoCl_2 \cdot 6H_2O$ increased the oil yield, while the transition metal iron acted as the activation center to accelerate the breakdown of chemical bonds in the organic matter of oil shale. Zou et al. [10] studied the catalytic effect of metal chlorides on the pyrolysis of lignite. The results showed that $CaCl_2$ and $ZnCl_2$ inhibited the conversion of organic matter into light species during the pyrolysis of lignite samples, whereas KCl, $NiCl_2$ and $CoCl_2$ promoted the conversion. Williams and Chishti [11] studied the effect of zeolite catalysts on the pyrolysis of Pakistan oil shale. It was shown that the catalysts markedly decreased the overall content of sulfur and nitrogen in the shale oil derived. Gai et al. [12] investigated the influence of inherent and additional pyrite on the pyrolysis of oil shale. Inherent pyrite was found to increase the oil yield, while additional pyrite promoted the production of volatiles. Bakr et al. [13] studied the role of pyrite during the pyrolysis process of kerogen. The results showed that the catalyst enhanced the formation of free radical, which might be attributed to the nascent sulfur produced during the conversion process of pyrite to pyrrhotite. At the same time, the conclusions reached by other researchers about the catalytic effect of pyrite on oil shale pyrolysis are different. For example, Metecan et al. [14] studied the effect of pyrite catalyst on the hydroliquefaction of Göynük oil shale in the presence of toluene. Pyrite was shown to have no noticeable effect on oil shale conversion and extract yield, however, it increased considerably the conversion rate. Vučelić et al. [15] investigated the catalytic effect of indigenous minerals on the pyrolysis of Aleksinac oil shale organic matter. It was suggested that changes in organic matter could be attributed to thermal rather than to catalytic cracking. The above results allowed one to conclude that catalysts do accelerate the pyrolysis process or increase the product yields, but their catalytic effect on the pyrolysis of kerogens of different oil shales is different. Among the catalysts studied, transition metal salts have attracted considerable attention lately, due to their obviously high catalytic activity.

The resource of Jimsar oil shale found in Xinjiang Province, northwestern China has been estimated at over 1.15×10^{10} tons [16, 17] and has attracted ever-increasing attention in recent years. Previously, Pan et al. [18–22] have studied the influence of process conditions, heat transfer characteristics and inherent mineral matter on the pyrolysis of Jimsar oil shale. At present, little research is being conducted on the pyrolysis of Jimsar oil shale catalyzed by metal salts, especially transition metal salts. To have a deeper knowledge of Jimsar oil shale and maximize its oil production rate, in this study, three transition metal salts, namely Fe_2O_3, $CoCl_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$, were investigated for their catalytic performance during the oil shale pyrolysis process. First the performances of the catalysts were compared using a thermogravimetric (TG) analyzer, then the most effective catalytic pyrolysis process was analyzed by thermogravimetry-mass spectrometry (TG-MS).

2. Material and methods

2.1. Oil shale samples

The oil shale samples used in this study were obtained from Jimsar, Xinjiang Province, northwestern China. The characteristics of Jimsar oil shale are given in Table 1.

Table 1. Characteristics of Jimsar oil shale, wt%, ad[a]

	Characteristic	Average	δ
Proximate analysis	Moisture	1.88	0.024
	Volatile matter	18.03	0.039
	Fixed carbon	3.15	0.021
	Ash	76.94	0.037
Ultimate analysis	C	15.78	0.014
	H	2.55	0.025
	O	4.54	0.021
	N	0.40	0.021
	S	0.35	0.001
Fischer analysis	Oil content	7.0	
	Water	2.0	
	Gas	2.03	
	Semi-coke	88.97	

[a] All the results are the mean of three experiments
δ – standard deviation of three experiments.
ad – air dried.

For the study, the samples were crushed and screened by the grinding machine to 100-mesh size. Fe_2O_3, $CoCl_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ were used as catalysts. According to literature, pyrite has been usually used to catalyze the pyrolysis of coal and oil shale, while sulfur may cause environmental pollution [12–14]. Therefore, we took Fe_2O_3 as a catalyst instead of pyrite. All the catalysts used were analytically pure. The metal ions in the catalysts accounted for 1% of the sample, by weight. The oil shale particles of desired size were distributed evenly in the three kinds of solutions containing different catalysts. Then the solutions were stirred in a magnetic stirrer at 80 °C until becoming sticky. Afterwards the solutions were dried in a hot-air dryer at 105 °C for 10 hours and eventually ground to 100 mesh.

2.2. Experimental procedure

The thermogravimetric/differential thermal-mass spectrometric (TG/DT-MS) analyses were carried out using a Netzsch STA 449f3 analyzer, to screen out the best-performing catalyst first. In the 2nd step, about 10 mg samples were distributed uniformly in the crucible and heated from ambient temperature to 1000 °C at a heating rate of 5, 10, 15 and 20 °C/min. The flow rate of argon as carrier gas was maintained at 60 ml/min during the whole experimental process. The derived products were swept into a mass spectrometer through the capillary column connected with the TG analyzer. The temperature of the capillary was kept at 255 °C to avoid plugging. The weight loss of sample was continuously recorded as a function of temperature and time through the TG analyzer during the pyrolysis process. The product components and their traces were targeted by a single ion monitoring of MS.

3. Results and discussion

3.1. Comparison of catalytic effect

Figure 1 shows the total weight loss curves of the oil shale samples during pyrolysis with and without catalysts at the heating rate of 10 °C/min.

The weight loss of raw oil shale (OS-R) and samples with Fe_2O_3 (OS-Fe) and $MnSO_4 \cdot H_2O$ (OS-Mn) occurred in three clearly differentiated stages. In stage I, below 300 °C, the weight loss was attributed to the evaporation of external moisture and interlayer water from clay minerals. In stage II, in the median temperature range (300–550 °C), the weight loss happened due to the decomposition of kerogen and bitumen. In stage III, at a temperature from 550 to 1000 °C, the final weight loss was mostly attributed to the thermal
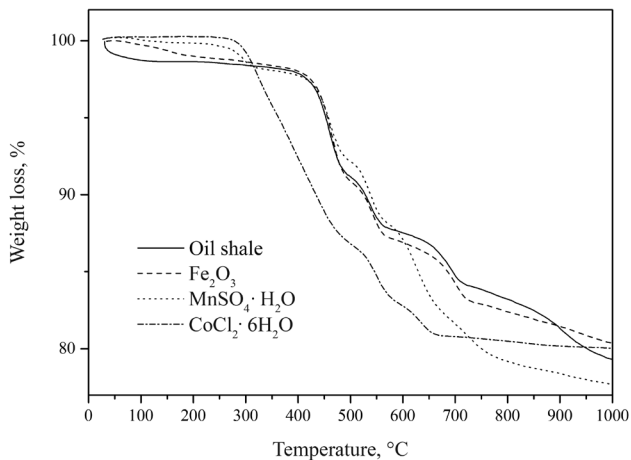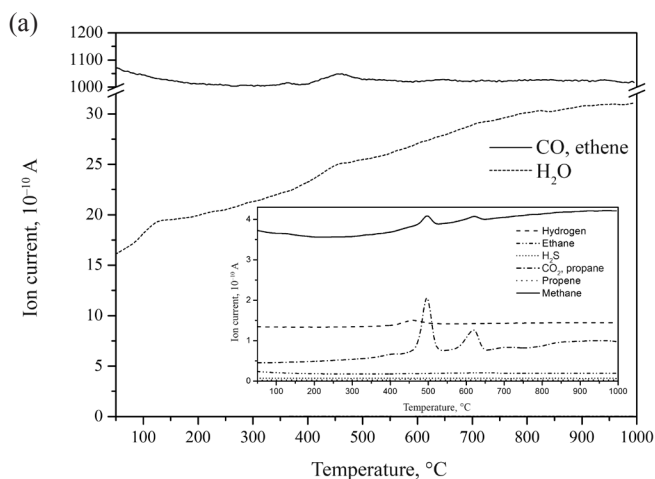

Fig. 1. TGA curves of oil shale samples during pyrolysis with and without catalysts.
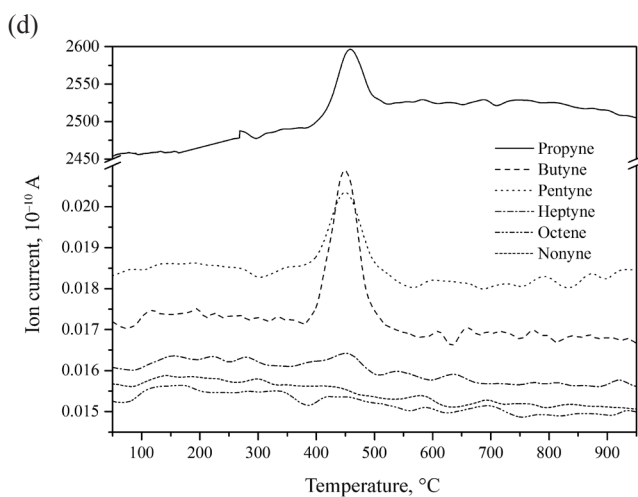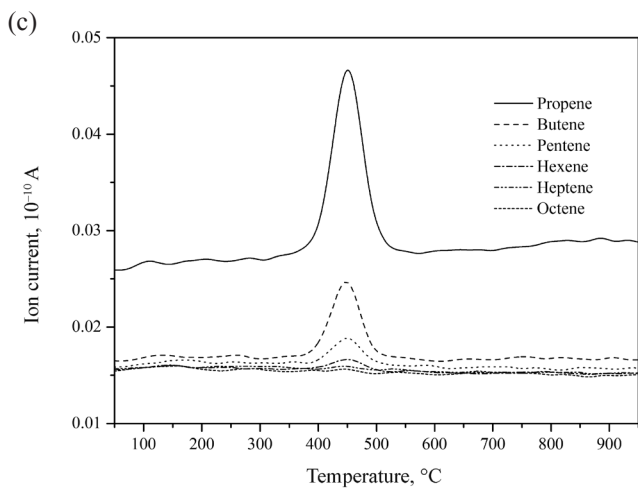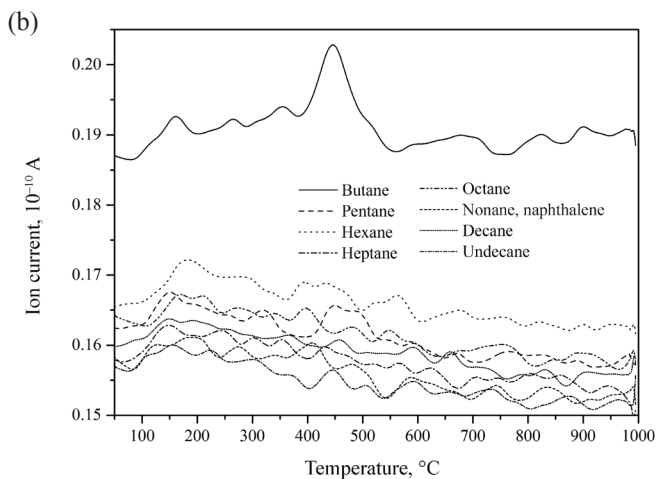
decomposition of inorganic minerals. The very small weight loss of the sample with $CoCl_2 \cdot 6H_2O$ (OS-Co) in stage I could be explained by that the catalyst absorbed the water released by the sample at a low temperature. The catalyst was added by the impregnation method and was dried in a 105 °C hot-air dryer, becoming partially dehydrated. When the water in the sample evaporated, it was immediately absorbed by the catalyst. The weight loss of the OS-Co sample occurred mostly in stage II, while above 650 °C, the weight of the sample almost remained constant. This could mean that the decomposition of minerals was finished by 650 °C and they decomposed together with kerogen and bitumen. From Figure 1 it can be seen that the catalytic effect of Fe_2O_3 was low at a temperature above 500 °C. At the same time, $MnSO_4 \cdot H_2O$ exerted a certain catalytic effect, especially in the stage of minerals decomposition. During the pyrolysis process, the catalytic effect of $CoCl_2 \cdot 6H_2O$ was the highest, causing the initial temperature of decomposition to decrease from 435 to 330 °C and the temperature range from 435–1000 °C to 330–650 °C. The effectiveness of the above catalysts during the pyrolysis process of Jimsar oil shale samples decreased in the following order: $CoCl_2 \cdot 6H_2O > MnSO_4 \cdot H_2O > Fe_2O_3$. Therefore further in this study, $CoCl_2 \cdot 6H_2O$ served as a catalyst to determine the yields of pyrolysis products.

3.2. TG-MS analysis

Using the ion current signal, the evolution rates of different compounds can be tracked, while the intensity of the signal represents the concentration of a gaseous constituent at different temperatures. The areas under iron density peaks were integrated to estimate the amount of each compound [18, 23, 24].

We analyzed 34 products with relatively high yield among the total 64 compounds targeted for all the experiments. Figure 2 shows the evolution signals of different types of compounds at a heating rate of 5 °C/min during pyrolysis with $CoCl_2 \cdot 6H_2O$.

(b)

(c)

(d)

(e)

Fig. 2. Evolution signals of different types of compounds at the heating rate of 5 °C/min during pyrolysis with $CoCl_2 \cdot H_2O$.

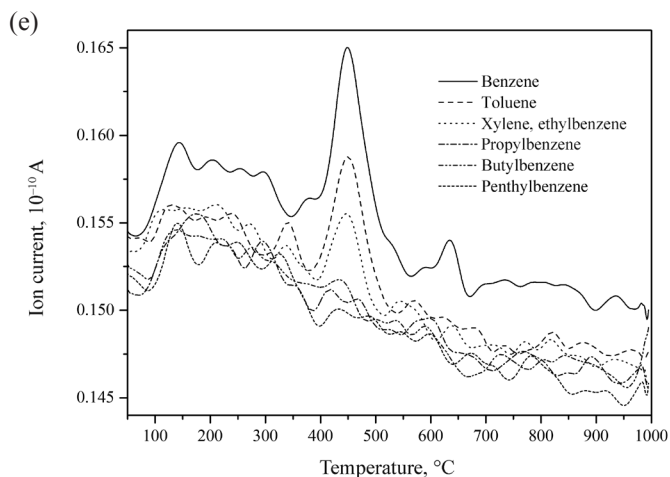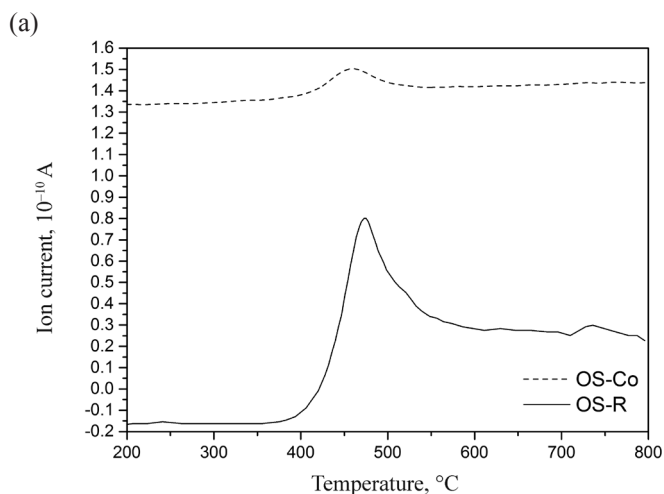Most compounds such as alkanes, alkenes, alkynes, alkyl benzenes, CO/ethene, H_2O and polyaromatics were generated in the temperature range of about 350–550 °C. Two compounds, CO/ethene and propyne, had the highest yield.

Figure 3 shows comparatively the yields of H_2 and CO/ethene of OS-R and OS-Co at a heating rate of 5 °C/min.
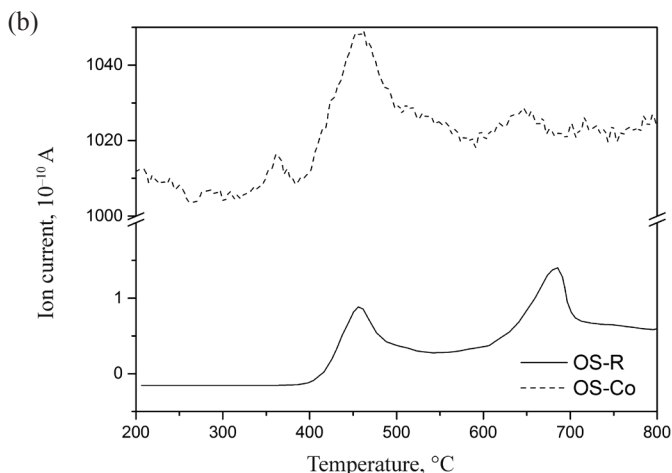
(a)

(b)

Fig. 3. Comparison of typical product yields of oil shale pyrolysis with and without catalyst at the heating rate of 5 °C/min: (a) H_2 and (b) CO/ethene.

The figure reveals that the yields of H_2 and CO/ethene were increased about 14.44 and 5021 times, respectively. Table 2 gives the ratios of relative areas of ion current response to products evolved from OS-R and OS-Co at a heating rate of 5 °C/min.

Table 2. Yield ratios of products of oil shale pyrolysis with and without catalyst at a heating rate of 5 °C

Sample	Alkanes/alkenes	Alkanes/alkynes	Alkanes/cyclics and aromatics	Alkanes/hydrogen
OS-R	0.81	1.67	10.13	2
OS-Co	12.07	0.0005	1.44	0.04

On the basis of Figure 3 and Table 2, it can be concluded that for OS-Co, the yields of all the products were remarkably increased, while the increase in the yield of alkanes was lower than that of alkynes, cyclic alkanes and aromatics, but the case was opposite with alkenes.

Usually, kerogen is initially decomposed to produce pyrolytic bitumen and then the bitumen is cracked to oil, gas and char products [12, 25–27]. In our experiments, $CoCl_2 \cdot 6H_2O$ was added using the pickling process, making Co^{2+} attached to the surface or interstices of kerogen. There could be formed

an electrostatic field if there are some cations or anions near Co^{2+}. Then the bonds in the kerogen molecule, such as C–H, C–O, C–S and C–N, would be polarized dynamically, giving rise to the induced reaction. This induced reaction was transferred along the kerogen molecule chain to another polarized bond adjacent to the C–C bond, which would be polarized and even broken. Previously Pan et al. [18] had concluded that Jimsar oil shale kerogen was of type I with typical characteristics of methylene carbon. Therefore we think that ethene accounted for the major part of CO/ethene. Because of the induced reaction, most of the methylene carbon functional group was detached from the large molecules of oil shale and dehydrogenated. This might be the reason behind the formation of a high amount of propyne.

Knowingly, the amount of water in the oil shale pyrolysis process increases with increasing temperature. In our opinion, this might be related to the electronic structure of the Co metal. There is an empty orbit of the d electron in Co, which can pair with the s electron in H [28], generating a large number of hydrogen radicals. On the other hand, metal chlorides mainly promoted the decomposition of carboxylic acid and the cleavage of C–O bonds [23], while hydrogen radicals might combine with oxygen radicals to form water. Thirdly, based on Figure 1, it can be concluded that the catalyst can also accelerate the decomposition of mineral salts. It means that the structural water was released during the pyrolysis of kerogen and bitumen. Therefore, with the catalyst and increasing temperature, the formation rate and amount of H_2O increased.

3.3. Influence of heating rate

The TG curves of Jimsar oil shale during pyrolysis with $CoCl_2 \cdot 6H_2O$ at four heating rates are shown in Figure 4.

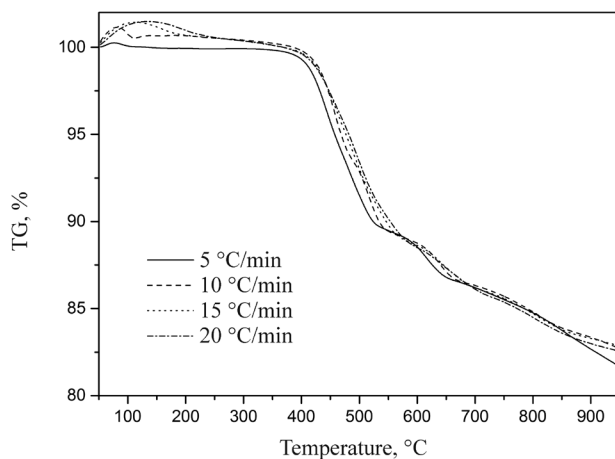Fig. 4. Weight loss (TG) curves of oil shale during pyrolysis at four heating rates.

The figure reveals that heating rate influenced the pyrolysis process slightly, whereas with increasing heating rate, the pyrolytic reaction shifted to a higher range of temperature.

Comparison of the amounts of each compound obtained at different heating rates provides information about the influence of heating rate on the pyrolysis process. Figure 5 reveals that the yield of each product changes with heating rate.
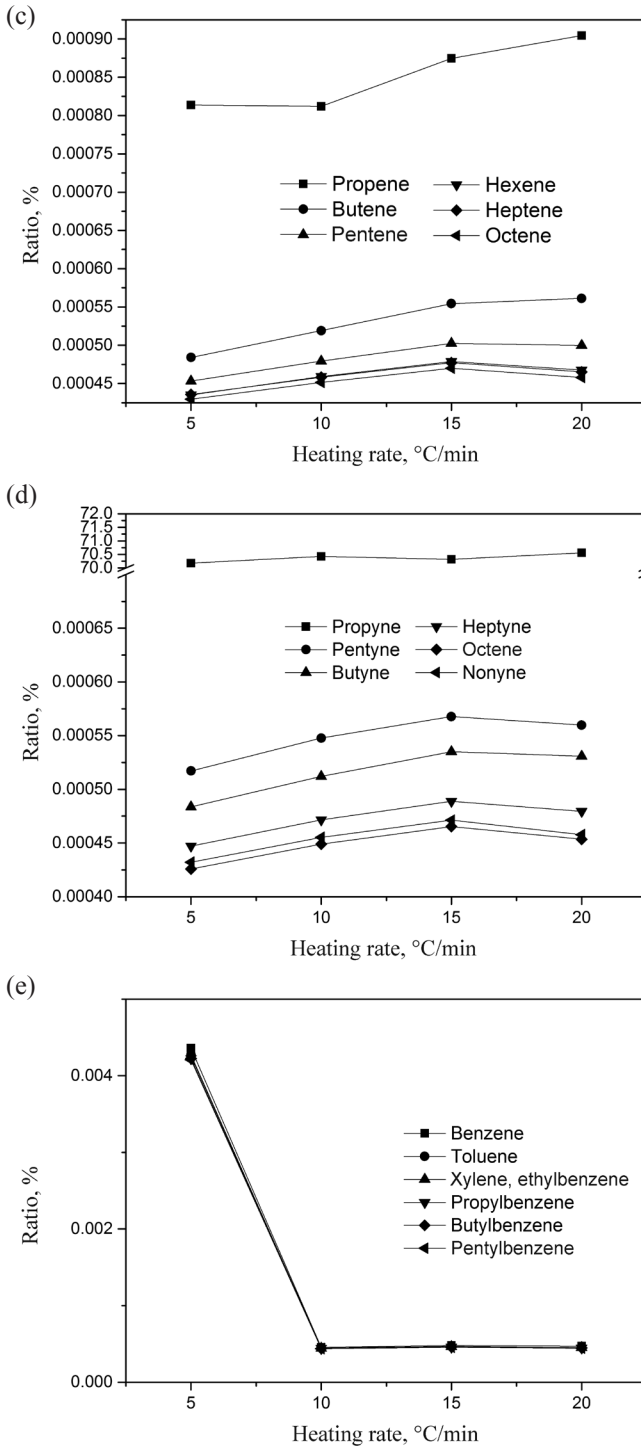
(c)

(d)

(e)

Fig. 5. Effect of heating rate on the products yield.

The ordinate represents the percentage of the yield of a certain product of the total yield of the products. It can be seen that with increasing heating rate, the yields of alkenes and alkynes increased, those of H_2O, alkanes and aromatic hydrocarbons decreased, whereas the yields of CO, H_2S, ethane, propene and CO_2/propane changed but a little. According to literature, the methylene carbon functional group accounts for almost 68.05% of Jimsar oil shale [18]. Attached to the surface or interstices of kerogen, Co^{2+} accelerated the polarization and breakage of the bonds, especially C–C bonds, generating a high amount of light unsaturated hydrocarbons. With increasing heating rate, the activation energy required for the polarization of the bonds fracture was satisfied in a shorter time. This might be the reason behind the increase in the yield of alkenes and alkynes with increasing heating rate. In addition, with increasing heating rate, the temperature difference between the surface and the central part of the oil shale particle became greater and greater. Sticky bitumen clogged the pores of oil shale particles, obstructing the escape of internal gas and accelerating the deposition of carbon. Therefore, the catalytic effect of a transition metal could be decreased with increasing heating rate. With $CoCl_2 \cdot 6H_2O$ as a catalyst, the optimal heating rate of Jimsar oil shale should be 5 °C.

Co is a kind of so-called Zigler-Natta (Z-N) catalysts [29]. In oil shale, a catalytic center is mainly fixed to its olefinic substrate and can thus establish a steady-state distribution of interconvertible intermediates through the reversible steps as expressed in Equation (1):

$$M — H(R) \rightleftharpoons M \quad H(R) \tag{1}$$

Equation (2) describes an irreversible hydrogenolysis step as follows:

$$\overset{R}{\underset{|}{M}} + H_2 \longrightarrow \overset{H}{\underset{|}{M}} + RH, \tag{2}$$

where R denotes a hydrocarbon unit alkyl or cycloalkyl bonded to the metal (M) through a metal carbon σ bond. The two equations define a catalytic cycle for the generation of methane from hydrogen and a normal alkane. Z-N metal salts, in an anhydrous anaerobic atmosphere, catalyze the above reactions with remarkable facility [29]. At the same time, the catalytic activity of the catalyst is related not only to the conditions mentioned above, but also to the temperature, pressure and reaction time [30]. Therefore, with increasing heating rate, the time left for the addition reaction to take place (Eq. (2)) is getting shorter and shorter, enabling no conversion of unsaturated hydrocarbons to alkanes. This might be the reason for the increase of alkenes and alkynes yield and the decrease of alkanes yield with increasing heating rate.

4. Conclusions

Three transition metal salts, namely Fe_2O_3, $CoCl_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$, as candidate catalysts were investigated for their catalytic performance in the pyrolysis process of Jimsar oil shale. First the pyrolysis behaviors of the catalysts were compared using a thermogravimetric analyzer, then the most effective pyrolysis process was analyzed by thermogravimetry-mass spectrometry.

The main conclusions are summarized as follows:

1. The three catalysts had a certain catalytic effect on the pyrolysis of Jimsar oil shale, while $CoCl_2 \cdot 6H_2O$ performed best.
2. With $CoCl_2 \cdot 6H_2O$, the initial reaction temperature was reduced by about 100 °C and the temperature range was reduced from 435–1000 °C to 330–650 °C.
3. The yields of CO/ethene and propyne were the highest, whereas ethene accounted for the major part of CO/ethene.
4. With increasing heating rate, the yields of alkenes and alkynes increased, those of H_2O, alkanes and aromatic hydrocarbons decreased, and the yields of CO, H_2S, ethane, propene and CO_2/propane changed but a little.
5. With $CoCl_2 \cdot 6H_2O$ as a catalyst, 5 °C/min proved to be the optimal heating rate for Jimsar oil shale pyrolysis.

Acknowledgements

REFERENCES

1. Coetzee, S., Neomagus, H., Bunt, J. R., Everson, R. C. Improved reactivity of large coal particles by K_2CO_3 addition during steam gasification. *Fuel Process. Technol.*, 2013, **114**(3), 75–80.
2. Jaffri, G.-e-R., Zhang, J. Y. Catalytic gasification characteristics of mixed black liquor and calcium catalyst in mixing (air/steam) atmosphere. *J. Fuel Chem. Technol.*, 2008, **36**(4), 406–414.
3. Öztas, N. A., Yürüm, Y. Pyrolysis of Turkish Zonguldak bituminous coal. Part l. Effect of mineral matter. *Fuel,* 2000, **79**(10), 1221–1227.
4. Ye, D. P., Agnew, J. B., Zhang, D. K. Gasification of a South Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. *Fuel*, 1998, **77**(11), 1209–1219.

5. Öztas, N. A., Yürüm, Y. Effect of catalysts on the pyrolysis of Turkish Zonguldak bituminous coal. *Energy Fuels*, 2000, **14**(4), 820–827.

6. Quyn, D. M., Wu, H., Hayashi, J. I., Li, C. Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part IV. Catalytic effects of NaCl and ion-exchangeable Na in coal on char reactivity. *Fuel*, 2003, **82**(5), 587–594.

7. Wu, H. W., Li, X. J., Hayashi, J. I., Chiba, T., Li, C. Z. Effects of volatile–char interactions on the reactivity of chars from NaCl-loaded Loy Yang brown coal. *Fuel*, 2005, **84**(10), 1221–1228.

8. Yu, J. L., Tian, F. J., Chow, M. C., McKenzie, L. J., Li, C. Z. Effect of iron on the gasification of Victorian brown coal with steam: enhancement of hydrogen production. *Fuel*, 2006, **85**(2), 127–133.

9. Jiang, H. F., Song, L. H., Cheng, Z. Q., Chen, J., Zhang, L., Zhang, M. Y., Hu, M. J., Li, J. N., Li, J. F. Influence of pyrolysis condition and transition metal salt on the product yield and characterization via Huadian oil shale pyrolysis. *J. Anal. Appl. Pyrol.*, 2015, **112**, 230–236.

10. Zou, X. W., Yao, J. Z., Yang, X. M., Song, W. L., Lin, W. G. Catalytic effects of metal chlorides on the pyrolysis of lignite. *Energy Fuels*, 2007, **21**(2), 619–624.

11. Williams, P. T., Chishti, H. M. Two stage pyrolysis of oil shale using a zeolite catalyst. *J. Anal. Appl. Pyrol.*, 2000, **55**(2), 217–234.

12. Gai, R. H., Jin, L. J., Zhang, J. B., Wang, J. Y., Hu, H. Q. Effect of inherent and additional pyrite on the pyrolysis behavior of oil shale. *J. Anal. Appl. Pyrol.*, 2014, **105**, 342–347.

13. Bakr, M. Y., Yokono, T., Sanada, Y., Akiyama, M. Role of pyrite during the thermal degradation of kerogen using in situ high-temperature ESR technique. *Energy Fuels*, 1991, **5**(3), 441–444.

14. Metecan, İ. H., Sağlam, M., Yanik, J., Ballice, L., Yüksel, M. The effect of pyrite catalyst on the hydroliquefaction of Göynük (Turkey) oil shale in the presence of toluene. *Fuel*, 1999, **78**(5), 619–622.

15. Vučelić, D., Marković, V., Vučelić, V., Spiridonović, D., Jovančićević, B., Vitorović, D. Investigation of catalytic effects of indigenous minerals in the pyrolysis of Aleksinac oil shale organic matter. *Org. Geochem.*, 1992, **19**(4–6), 445–453.

16. Brendow, K. Global oil shale issues and perspectives. *Oil Shale*, 2003, **20**(1), 81–92.

17. Bunger, J. W., Crawford, P. M., Johnson, H. R. Is oil shale America's answer to peak-oil challenge? *Oil Gas J.*, 2004, **102**(30), 16–24.

18. Pan, L. W., Dai, F. Q., Li, G. Q., Liu, S. A TGA/DTA-MS investigation to the influence of process conditions on the pyrolysis of Jimsar oil shale. *Energy*, 2015, **86**(15), 749–757.

19. Pan, L. W., Dai, F. Q., Tian, Y. Q., Zhang, F. H. Experimental investigation of the sphericity of irregularly shaped oil shale particle groups. *Adv. Powder Technol.*, 2015, **26**(1), 66–72.

20. Pan, L. W., Dai, F. Q., Huang, J. N., Liu, S., Zhang, F. H. Investigation of the gas flow distribution and pressure drop in Xinjiang oil shale retort. *Oil Shale*, 2015, **32**(2), 172–185.

21. Pan, L. W., Dai, F. Q., Huang, J. N., Liu, S., Zhang, F. H. Study of a new gas inlet structure designed for Xinjiang oil shale retort. *Oil Shale*, 2016, **33**(1), 69–79.

22. Pan, L. W., Dai, F. Q., Huang, J. N., Liu, S., Li, G. Q. Study of the effect of mineral matters on the thermal decomposition of Jimsar oil shale using TG-MS. *Thermochim. Acta*, 2016, **627–629**, 31–38.

23. Liu, L. L., Kumar, S., Wang, Z. H., He, Y., Liu, J. Z., Cen, K. F. Catalytic effect of metal chlorides on coal pyrolysis and gasification part I. Combined TG-FTIR study for coal pyrolysis. *Thermochim. Acta*, 2017, **655**, 331–336.

24. Tiwari, P., Deo, M. Compositional and kinetic analysis of oil shale pyrolysis using TGA-MS. *Fuel*, 2012, **94**, 333–341.

25. Haddadin, R. A., Mizyed, F. A. Thermogravimetric analysis kinetics of Jordan shale. *Ind. Eng. Chem. Proc. Des. Dev.*, 1974, **13**(4), 332–336.

26. Williams, P. F. V. Thermogravimetry and decomposition kinetics of British Kimmeridge Clay oil shale. *Fuel*, 1985, **64**(4), 540–545.

27. Thakur, D. S., Nuttall Jr., H. E. Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry. *Ind. Eng. Chem. Res.*, 1987, **26**(7), 1351–1356.

28. Xie, X. X., Luo, J. C., Ge, Q. M., Dai, A. J., Zou, T. The influence of catalyst on coal pyrolysis characteristics. *Coal Chemical Industry*, 2015, **43**(4), 38–42 (in Chinese with English abstract).

29. Mango, F. D. Transition metal catalysis in the generation of petroleum and natural gas. *Geochim. Cosmochim. Acta*, 1992, **56**(1), 553–555.

30. Luo, W. G. Wen, L. Y., Yu, F., Pan, Z. Y., Zong, B. N. Study on the hydrogenation of isooctene to isooctane over Ziegler-Natta catalyst. *Acta Petrolei Sinica (Petroleum Processing Section)*, 2007, **23**(6), 86–90 (in Chinese, with English abstract).