Study on hydro-liquefaction kinetics of thermal dissolution soluble fraction from Shenfu sub-bituminous coal

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HIGHLIGHTS

- TDSF is almost completely liquefied at 380 °C with high yield of oil + gas.
- The model of hydro-liquefaction of TDSF includes series and parallel reactions.
- The regressive reaction is ruled out in the model.
- TDSF to PA and PA to oil + gas are the main reactions.
- Oil + gas are mainly formed from the reaction of PA to oil + gas.

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ABSTRACT

Thermal dissolution (TD) of coal and hydro-liquefaction of the thermal dissolution soluble fraction (TDSF) with a high activity catalyst is one of effective high efficient hydro-liquefaction of coal techniques. In this study, a Chinese Shenfu (SF) sub-bituminous coal was thermally dissolved, and the TDSF obtained was further hydro-liquefied with Ni–Mo-S/Al$_2$O$_3$ catalyst. Based on the hydro-liquefaction results, a model including series and parallel reactions was established for the hydro-liquefaction of TDSF catalyzed by Ni–Mo-S/Al$_2$O$_3$, and the regressive reactions were ruled out in the model. From the kinetic parameters calculated, it suggested that the regressive reactions including the char formation reactions were negligible in the hydro-liquefaction of TDSF catalyzed by Ni–Mo-S/Al$_2$O$_3$. The reactions of TDSF to preasphaltene and preasphaltene to oil + gas predominated the formation of oil + gas. Ni–Mo-S/Al$_2$O$_3$ could decrease the activation energy of preasphaltene to oil + gas reaction, thus promoting the formation of oil and gas in the catalytic hydro-liquefaction of TDSF.

1. Introduction

Thermal dissolution (TD) of coal has been becoming one of the most important ways for the cleaning utilization of low rank coals (LRCs). High thermal dissolution soluble yield (TDSY) of LRCs can be obtained at mild temperature with some organic single or mixed solvents. In order to obtain high yield of thermal dissolution soluble fraction (TDSF) at a mild temperature and to decrease the emission of greenhouse gases, co-thermal dissolutions of LRC and biomass are also carried out. The TDSFs from LRCs have a wide use. They can be combusted directly in gas turbines to obtain a higher net power output thus reducing CO$_2$ emissions, [1–5]

because the ash content in TDSFs is lower than 200 ppm. The TDSFs can also be used in low temperature catalyzed gasification [6,7] due to the catalyst used in this process being reusable. Koyano et al. [8] found that the catalyst used in the hydro-liquefaction of TDSF could be recycled used five times and no deactivation of catalyst was detected. This is because TDSF consists of soluble components with free of ash, and the catalyst used in the hydro-liquefaction of TDSF can be recovered easily. We also find that the TDSF from a Chinese sub-bituminous Shenfu (SF) coal has a good hydro-liquefaction activity with high yield of oil, and the solid catalyst BF$_3$/SBA-15 used in the hydro-liquefaction of the TDSF is reusable at least 4 times [9]. Based on the results, a new pathway for high-efficiency coal liquefaction is advanced that LRC is thermally dissolved at a mild temperature to give high yield

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Nomenclature

TD	thermal dissolution	THFI	THF insoluble fraction
TDSF	thermal dissolution soluble fraction	Pa	preasphaltene
SF	Shenfu	As	asphaltene
LRC	low rank coal	Un	unreacted TDSF
TDSY	thermal dissolution soluble yield	Og	oil + gas
1-MN	1-methyl naphthalene	k	rate constant
THF	tetrahydrofuran	Ea	apparent activation energy

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of TDSF, and then the TDSF is hydro-liquefied using a reusable high active catalyst to obtain high yield of oil.

Study on the kinetics of coal liquefaction has an important role for mechanism understanding, reactors design and process optimization. Due to the complexity of coal structure and the diversity of products from coal liquefaction, the liquefaction products are normally divided into several lumped parameters based on the solubility in various solvents, and the lumped parameter method is widely used to study the kinetics of coal liquefaction. Weller et al. [10,11] believed that coal liquefaction was a simple series reaction scheme. From coal to oil the reaction would pass through an intermediate product: asphaltene. A combination of series and parallel reactions model was proposed by Cronauer et al. [12] with assuming each reaction to be first order, and four lumped parameters, i.e. preasphaltene, asphaltene, oil and gas were included in the liquefaction products. Shalabi [13] believed that lumping oil and gas as one parameter in Cronauer's model could descript the coal liquefaction process better. Based on a series of irreversible and pseudo first-order reactions mechanism, Kadim et al. [14] and Angelov et al. [15] proposed five models which were well fitted experimental results for the coal liquefaction at different temperatures. Sharma et al. [16] suggested a consecutive reaction scheme for the liquefaction of coal with second-order kinetic models.

Among these coal liquefaction kinetic models, retrogressive reactions especially char formation were paid little attention. Li et al. [17] studied on the kinetics of Shenhua coal liquefaction, they divided the coal into easy reactive, hard reactive and un-reactive three parts and two lumped parameters, i.e. preasphaltene + asphaltene and oil + gas were used in the model. We have proposed a new kinetic model for SF coal liquefaction catalyzed by SO_4^{2-}/ZrO_2 solid acid catalyst using the kinetic lump method [18]. Some retrogressive reactions such as oil + gas to asphaltene and asphaltene to preasphaltene and the formation of char from asphaltene and preasphaltene have been considered. The model agreed well with the experimental data at the range of experimental conditions, suggesting that retrogressive reactions real existed in the liquefaction of SF coal, especially at high liquefaction temperature. Ikeda [19] et al. also proposed a reaction kinetic model of coal liquefaction with retrogressive reaction.

Although many researches about catalytic kinetics of coal liquefaction have been carried out, however kinetic study on the catalytic liquefaction of TDSF has no any report based on author's knowledge. The hydro-liquefaction properties of TDSF are quite different from that of raw coal. TDSF gave much higher of liquefaction conversion and oil yield than the raw coal mentioned above, therefore the liquefaction mechanisms between coal and the TDSF are different. In this study, the catalytic hydro-liquefaction kinetics of a TDSF from SF coal using a high hydrogenation activity catalyst of Ni–Mo–S/Al₂O₃ was investigated. A kinetic model of hydro-liquefaction of TDSF catalyzed by Ni–Mo–S/Al₂O₃ was estimated, and some kinetic parameters were obtained. The model predicted values were fitted excellently with the experimental data.

2. Experimental

2.1. Feedstocks and solvents

The coal used in this study is a Chinese subbituminous SF coal. It was ground to a size less than 100 μm, and followed by desiccation in vacuum at 80 °C overnight before use. The ultimate and proximate analyses of SF coal are shown in Table 1. The TDSF was obtained from the TD of SF coal at 360 °C using 1-methyl naphthalene (1-MN) with addition of 10 (v)% methanol (1-MN + 10% MT) as TD solvent. The description of TD procedure in details are shown elsewhere [5,20]. The TD yield of TDSF is 67%. The ultimate analysis of TDSF obtained is also shown in Table 1. All solvents used are commercial purchased without further purification and the purity is higher than 99.5%.

2.2. Catalyst preparation and characterization

The catalyst used in the hydro-liquefaction of TDSF is a self-prepared catalyst Ni–Mo-S/Al₂O₃. It was prepared as following: dissolving the required amounts of $(NH_4)_6Mo_7O_{24}·4H_2O$ and Ni $(NO_3)_2·6H_2O$ in distilled water with adding a certain amount of Al₂O₃, the mixture obtained was then evaporated at 60 °C with stirring to remove water. After drying at 110 °C overnight and calcining at 500 °C for 4 h, the product was then reduced and sulphided under H₂ flow with addition of 0.02 ml/min of CS₂ at 400 °C for 2 h and aged with N₂ (containing 1% O₂) flow for 7 h. The catalyst obtained is called as Ni–Mo-S/Al₂O₃.

NH₃ temperature programmed desorption of the catalyst was carried out using a Quantachrome instrument (ChemBET 3000). Ni–Mo-S/Al₂O₃ catalyst (50 mg) was heated to 550 °C in pure He at a rate of 10 °C/min, and kept at 550 °C for 0.5 h, then cooled to 80 °C. Pure He flow was switched to 10% NH₃/He (40 mL/min) for 0.5 h. Then NH₃/He flow was switched to pure He (40 mL/min) for 0.5 h at 80 °C. Finally, the catalyst was heated from 80 °C to 600 °C at a rate of 10 °C/min, and the NH₃ temperature programmed desorption curve was recorded as shown in Fig. 1. It can be observed that there is a broad peak at the temperature range from 170 °C to 550 °C, indicating Ni-Mo-S/Al₂O₃ catalyst has the weak and moderately strong acid sites. The main acid sites of the catalyst are the weak acids since most of the adsorbed NH₃ desorbed at about 250 °C.

2.3. Hydro-liquefaction and product fractionation

The hydro-liquefaction kinetic experiments of TDSF were carried out in a 30 ml tube reactor as shown in details elsewhere [18]. Briefly, 0.5 g of TDSF loaded with 0.05 g catalyst together with 1 ml of tetralin and a shaker were charged into the reactor. The initial hydrogen pressure was set to 5.0 MPa. The reactor was heated by a eutectic salt bath, which had been heated to 5 °C above the desired temperature so as to the temperature of reactants in the