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Liquid Hydrocarbon Fuels from Catalytic Cracking of Waste Cooking Oils Using Basic Mesoporous Molecular Sieves K_2O/Ba-MCM-41 as Catalysts

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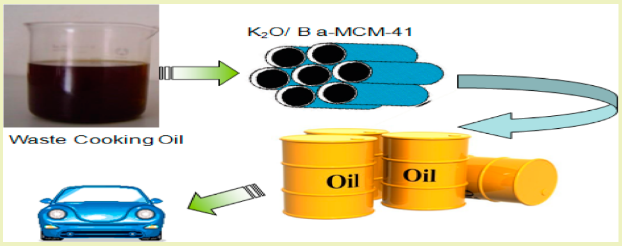
Supporting Information

ABSTRACT: Mesoporous molecular sieves K_2O/Ba-MCM-41, which feature base sites, were prepared under hydrothermal conditions. The structure, base properties, and catalytic activity of the mesoporous molecular sieves as heterogeneous catalysts for the cracking of waste cooking oil (WCO) were then studied in detail. K_2O/Ba-MCM-41 exhibited higher catalytic performance for the cracking of WCO than traditional base catalysts such as Na_2CO_3 and K_2CO_3. Moreover, the cracking of WCO generates fuels (main composition is C_{12}~C_{17} alkane or olefin) that have similar chemical compositions to diesel-based fuels, and K_2O/Ba-MCM-41 is of excellent stability. The catalyst could be recycled and reused with negligible loss in activity for four cycles. K_2O/Ba-MCM-41 is an environmentally benign heterogeneous basic catalyst for the production of liquid hydrocarbon fuels from low quality feed stocks.



KEYWORDS: *Waste cooking oils, Liquid hydrocarbon fuels, Catalytic cracking, Basic mesoporous molecular sieves, Heterogeneous catalysis*

INTRODUCTION

The generation of organic waste, such as food waste, livestock excretion, wastewater sludge, and butchery waste, continues to increase. But the treatment is only limited to abandoning, landfilling, and ocean disposal and has caused severe environmental pollution.[1] On the other hand, at present, the world is facing a crisis of fuel and energy. The available deposits of fossil fuels are continuously being depleted at an alarming rate while the prices are shooting up constantly. Hence, biodiesel will be a gift to meet the energy needs.[2] Therefore, effective utilization of organic waste cannot only solve the environmental question very well but also play a role in supplementing the energy demand. Waste cooking oil (WCO) is now considered as a potential source for producing biofuel.[3−7] The traditional esterification/transesterification reactions for the synthesis of biodiesel using an oil and acid base system has reached its saturation; also, the problem associated with the chemical synthesis of biodiesel involves a costly extraction procedure for glycerol recovery.[2] At the same time, WCO must be complexly pretreated to remove some impurities.[8] In recent years, there has been an increasing interest in catalytic cracking to produce biofuel.[9,10] This method applies thermal energy with appropriate catalysts to crack hydrocarbon; thus, it is not necessary to carry out any stages for the refining catalyst or separating product.[11] Catalysts for the pyrolysis process were usually solid catalysts with good shape selectivity and proper pore size. H-ZSM5, metal impregnated MCM-41, and Y zeolite catalysts have been used for hydrocarbon cracking.[12−15] However, the cracking oils in these studies exhibited a high carboxylic acid content (acid value was more than 120).[16] These undesirable products have a large effect on the corrosion value, cold filter plugging point, and freezing point of the biofuel.[17,18] To solve this question, we report the catalytic cracking of soybean oils using Na_2CO_3 or K_2CO_3 basic catalysts in a continuous mode.[18] The traditional base catalysts could decrease the acid value of biofuel, but the catalysts would decrease and the content of salt in the biofuel would increase, which would lead to corrosion of the equipment. Therefore, it is key to develop a new base solid catalyst to solve this problem.

Zeolites would be potential candidates due to their high thermal stability, shape selective properties caused by the microcrystalline structure, and ability to concentrate reactants

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Table 1. Effect of Different Catalysts on Reaction Results*

catalysts	conversion %	yield/% bio-oil	yield/% biogas	coke (%)	acid value mg KOH/g	CFPP (°C)[a]	FP (°C)[b]
blank	57.3	41.2	16.1	42.7	172	20.2	19.4
K_2CO_3	70.9	57.4	13.5	29.1	51	−8.2	−21.3
Na_2CO_3	73.7	57.6	16.1	26.3	54.5	−7.9	−19.6
HZSM-5	58.8	42.3	16.5	41.2	84	−2.8	−12.2
Si-MCM-41	66.4	45.7	20.7	33.6	90	−1.9	−11.9
Ba-MCM-41	70.2	55.7	14.5	29.8	62	−5.1	−15.3
K_2O/Ba-MCM-41[c]	79.2	63.2	16.0	20.8	43	−10.2	−26.0

[*] Reaction conditions: WCO 10 g, M(catalysts): M(WCO) = 1:50, 400 °C, 1.5 h. [a] CFPP means cold filter plugging point. [b] FP means freeing point. [c] Concentration of KNO_3 solvent = 11 wt % in the synthesis of catalyst

inside the pores.[19] For the creation of basic sites in zeolites and molecular sieves, several methods have been described so far.[20] Among them there are ion exchange with large alkali cations, e.g.,[21,22] isomorphous substitution of silicon by germanium in the zeolite framework[23] or the deposition of basic objectives in the cavities of the zeolite, e.g., the formation of sodium clusters by decomposition of sodium azide.[24] Whereas in the two former cases, no really strong basicity could be created, the alkali metal clusters produced by the latter approach turned out to be strongly basic but highly sensitive to oxygen. Hathaway and Davis demonstrated that relatively strong basic sites can be prepared by impregnating zeolites with cesium salts, particularly with cesium acetate, followed by calcination.[25] The zeolites as catalysts are only limited to relatively small molecules, particularly when they are loaded with cesium oxide clusters. Mesoporous molecular sieves of the M41S-type can help overcome these limitations due to their large pore sizes.[26] However, strong base material used to modify MCM-41 can react with silicon, which leads to the collapse of the mesoporous structure.[27] For this reason, there is little literature about using MCM-41 as support for basic catalysts.[28,29] Strong basic sites can appear, and the destruction to the zeolite structure can be avoided when the zeolite is loaded by using weak or middle basic materials as base precursors and is properly treated.[30] Therefore, we use different concentrations of KNO_3 solution to impregnate Si-MCM-41 to obtain basic site K_2O/Si-MCM-41 by calcination at 600 °C. K_2O/Si-MCM-41 is of a typical mesoporous structure, with crystallinity and long-range order. The catalytic properties of K_2O/Si-MCM-41 were investigated in the pyrolysis of polystyrene. The results were compared with those obtained using CaO, Si-MCM-41 and Al-MCM-41 as catalysts. It was shown that K_2O/Si-MCM-41 is of better catalytic activity.[28] However, K_2O/Si-MCM-41 is of poor catalytic activity on the cracking of WCO because of its low basicity. In this paper, first alkali metals are introduced into the skeleton of MCM-41 to prepare Ba-MCM-41 under hydrothermal conditions. Second, by using the impregnation method, K_2O is successfully supported on Ba-MCM-41. Then, by calcination, basic K_2O/Ba-MCM-41 is obtained.

To our knowledge, this is the first report on the use of mesoporous molecular sieves containing base sites as catalysts for the cracking of WCO into liquid hydrocarbon fuel. In this research, we design a K_2O/Ba-MCM-41 catalyst and study its catalytic activities for the production of liquid hydrocarbon fuel from WCO. The effect of several crucial variables such as concentration of KNO_3, reaction temperature, catalyst usage, and reaction time were also studied.

MATERIALS AND METHODS

Materials. WCO was obtained from commercial sources and used without further purification. Other materials, such as sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium silicate (Na_2SiO_3), hexadecyl trimethyl ammonium bromide (CTABr), barium chloride ($BaCl_2$), and potassium nitrate (KNO_3), were all purchased from Aldrich and directly used after dried without further purification.

Analysis of Cracking Oil. Gas chromatography−mass spectrometry (Agilent 6890N/5973N) was used to analyze the composition of the product. The separation was realized in a column of HP-5, 30 m × 0.25 mm × 0.25 μm, working between 70 °C (2 min) and 280 °C (20 min) at a heating rate of 5 °C/min. Different classes of compounds presented in the pyrolysates were confirmed by total ion chromatogram (TIC) and selected ion mass chromatogram analyses, in addition to fragmentation patterns and library matching (NIST). Identification was carried out according to pre-established criteria for analysis of the data. The dynamic viscosity was measured with SYD-265C viscometers (GB/T265−88), and the gross calorific value was measured with a Well 8000 fast automatic calorimeter. Moisture was tested by a SF 101 trace moisture analyzer. Cold filter plugging point and freezing point were tested by SYP 2007-2 and SYP 1008-5, respectively.

Characterization of Basic Mesoporous Molecular Sieves. X-ray powder diffraction patterns of the samples were obtained with a XB-3A instrument using monochromatic Cu Kα radiation (λ = 0.15418 nm). It was operated at 40 kV and 100 mA. The experimental conditions were at a step width of 0.02° and scan speed of 2°/min, and the diffraction was operated at narrow seam (diffraction region 2θ = 2−10°). The basic properties were measured by CO_2 adsorption at 30 °C, using a CHEMBET-3000 calorimeter coupled with a volumetric equipment.

Catalytic Cracking of WCO. Catalytic cracking experiments were carried out at temperatures ranging from 400 to 440 °C using a 250 mL glass vessel. WCO (W_1) and catalysts (W_2) were introduced into the reactor and then heated by an external electrical resistance at a heat rate of 20 °C/min. The temperature was measured at two positions (column temperature and bottom temperature) using calibrated thermocouples. When the temperature inside the reactor reached 400 °C, WCO cracked and vaporized. The vapor left the reactor through the rectification column at temperatures ranging from 400 to 440 °C and then entered the heat exchanger. Finally, the liquid fractions were weighed (W_3) and analyzed by GC-MS. Because the gas fractions could not be cooled and collected, the related yield can only be obtained by mass balance. The residue in the reactor including the coke and catalysts was weighed (W_4). The conversion (wt %) for WCO and yields (wt %) for coke and bio-oil are as follows

$$\text{Conversion}/\% = \frac{W_1 + W_2 - W_4}{W_1} \times 100\%$$

$$\text{Yield (coke)}/\% = \frac{W_4 - W_2}{W_1} \times 100\%$$

$$\text{Yield (bio-oil)}/\% = \frac{W_3}{W_1} \times 100\%$$

Preparation of Basic Mesoporous Molecular Sieves. Ba-MCM-41 was synthesized according to the hydrothermal method reported in the literature.[15] The molar ratio of the reactants was $BaCl_2:Na_2SiO_3$:silica gel:CTMABr:H_2O = 0.05:0.67:1:0.20:102.

Ba-MCM-41 was immersed into 5, 8, 11, 13, and 15 wt % KNO_3 for 30 min, respectively, and then the sample was filtrated and dried at 60 °C for 12h and calcined at 550 °C for 3 h to prepare K_2O/Ba-MCM-41. To investigate the effect of the impregnation concentration on the catalytic performance, here we marked the corresponding product as 5% K_2O/Ba-MCM-41, 8% K_2O/Ba-MCM-41, etc. The mesoporous structure of basic K_2O/Ba-MCM-41was determined by XRD (Supporting Information).

Stability Measurement. The reusability of the catalyst was studied using the used catalyst in the next consecutive reaction cycles. After being used each time, the catalyst was directly calcined in a muffle furnace at 550 °C for 3 h.

■ RESULTS AND DISCUSSION

Choice of Catalysts. The performance of different catalysts were investigated for the cracking of WCO and evaluated in terms of the yield of organic liquid product (bio-oil), coke yield, and other fuel properties such as acid value, CFPP(cold filter plugging point), and FP (freezing point). The detailed results are shown in Table 1. From Table 1, it can be seen that with the acid value increasing, the CFPP and FP of the cracking oil also increased. That is to say, the acid value had a close relationship with the cold flow properties.[17,18] The basic mesoporous molecular sieves K_2O/Ba-MCM-41 were of almost the same catalytic activity as the traditional base catalysts, such as Na_2CO_3 or K_2CO_3, according to the yield of bio-oil, acid value, CFPP, or FP. At the same time, the product showed good solubility in diesel at low temperature.

In order to identify the cracking products, the GC−MS analysis was carried out, and the results of the main components of the products obtained by different catalysts are shown in Table 2. These results show that the main components of the products are different for different catalysts. Using K_2O/Ba-MCM-41 as the catalyst, the main ingredient of pyrolysis oils were alkane or olefin compounds of around 16 total carbon numbers, and the total content was more than 70%, which was similar to diesel. However, using K_2CO_3 or Na_2CO_3 as catalysts, the distribution of the carbon number was very wide for the pyrolysis oil, and the content of one ingredient was not more than 20%. The properties of the pyrolysis oil for different catalysts were deeply studied, and the results are found in Table 3. For comparison purposes, Table 3 also displays the specified values for the petroleum-based fuel. The results show that the fuels derived from WCO using K_2O/Ba-MCM-41 as catalysts possessed acceptable values for the given properties when compared to those for the petroleum-based fuel. Therefore, K_2O/Ba-MCM-41 is an excellent catalyst for the catalytic cracking of WCO; its typical mesoporous structure could focus distribution of the product and improve the properties of fuels. The catalytic performance and catalytic stability of K_2O/Ba-MCM-41 would be researched as follows.

Catalytic Cracking of WCO by K_2O/Ba-MCM-41. According to Figure 1, the impregnation concentration of KNO_3 can greatly affect the catalytic activity of K_2O/Ba-MCM-41. With increasing concentration of KNO_3 from 5% to 11%, the conversion ascended from 72.3% to 79.2%, meanwhile the yield of bio-oil increased from 56% to 63.2%, which indicated that the increase in concentration of KNO_3 led to the increase in K_2O, and thus could enhance the basicity of catalyst. However, with increasing the concentration of KNO_3 from 11% to 15%, both the conversion and yield decreased due to the destruction of the mesoporous structure (Figure S2, Supporting Information).[26] At the same time, we use temperature-programmed desorption of CO_2 (CO_2-TPD) technology to determine the basicity of K_2O/Ba-MCM-41. In order to explain and elaborate the reaction mechanism catalyzed by basic sites, the CO_2-TPD technique was used to quantitative determination of basic sites, strength of basic sites, and its distribution in a heterogeneous catalyst.[31] Meanwhile, the contribution of the effect of metal loading on the basicity of Ba-MCM-41 has been examined by CO_2-TPD. The weak, medium. and strong catalyst basic sites were estimated from the area under their TPD curves at the temperature range of 320−500 °C, 500−750 °C, and >750 °C. The temperature ranges chosen for the weak, medium, and strong basic sites are those of the CO_2-TPD peaks observed in these temperatures for most catalysts. From Figure 2, it is shown that the total amount of CO_2 desorption from Ba-MCM-41 is very low, indicating the weak basic sites on its surface. In addition to this, the total amount of CO_2 desorption from K_2O-modified Ba-MCM-41 samples have increased and also showed the generation of basic sites on the surface of MCM-41 by post-synthesis impregnation with K_2O. It is worth noting that 11% K_2O/Ba-MCM-41 is of weaker basicity than 13% and 15% K_2O/Ba-MCM-41. Therefore, it suggested that the high dispersion of K_2O on Ba-MCM-41 support provides weak and medium basicity as well as a relatively high surface area of active phases.[32,33] Meanwhile, the cracking result of 11% K_2O/Ba-MCM-41 is better than other concentrations. As a result, the optimum impregnation concentration of KNO_3 for preparing K_2O/Ba-MCM-41 is 11 wt %.

The technological conditions of catalytic cracking WCO using K_2O/Ba-MCM-41 as catalyst were also tested in the present work, as shown in Table 4. The optimum technological conditions of catalytic cracking WCO were as follows: WCO 10

Table 2. Main Components of Cracking Oil from WCO*

catalysts	yield of bio-oil (%)	components	content (%)
Na_2CO_3	57.60	nonane	11.67
		decane	11.71
		dodecane	5.21
		1-tridecylene	9.63
		cetane	13.23
K_2CO_3	57.40	2-heptylene	6.12
		nonane	5.25
		cetane	7.88
		8-heptadecene	14.13
K_2O/Ba-MCM-41	63.20	1-laurylene	8.11
		dodecane	5.83
		tridecane	7.06
		tetradecane	7.44
		pentadecane	22.75
		cetane	10.10
		heptadecane	12.45
blank	41.20	1-octylene	6.81
		octane	6.53
		nonane	5.92
		4-decene	5.10
		hendecane	12.92

*Reaction conditions: WCO 10 g, M(catalysts): M(WCO) = 1:50, 420 °C, 1.5 h.

Table 3. Properties of Oil

fuel properties of catalysts	cracking oil, black	cracking oil, Na_2CO_3	cracking oil, K_2CO_3	cracking oil, K_2O/Ba-MCM-41	biodiesel[7]	$0^\#$ diesel	$93^\#$ gasoline
density g/cm^3	0.89	0.88	0.88	0.85	0.89	0.84	0.82
moisture content %	0.51	0.37	0.36	0.36	–	–	–
calorific value MJ/kg	30.24	38.08	38.45	41.45	39.00	43.56	44.00
dynamic viscosity mm^2/s, 40 °C	4.37	4.21	4.17	3.95	4.5	–	–
color	brown	yellow	yellow	faint yellow	–	faint yellow	colorless

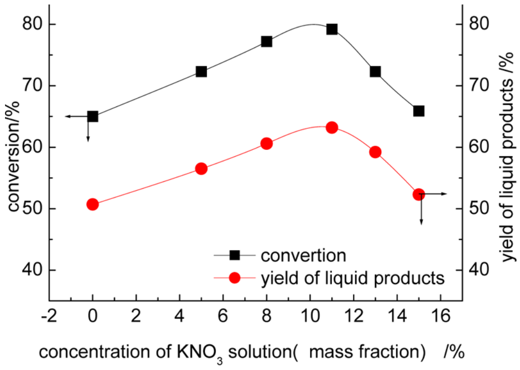

Figure 1. Effect of concentration of KNO_3 solution on catalytic activity of obtained K_2O/Ba-MCM-41 (WCO 10g, M(catalysts): M(WCO) = 1:50, 420 °C, 1.5 h).

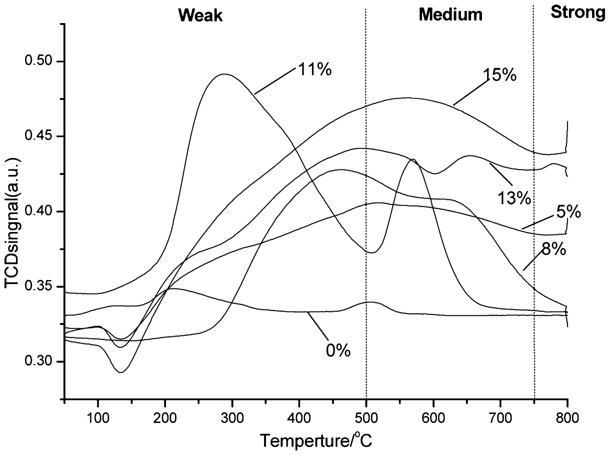

Figure 2. CO_2-TPD profiles of K_2O content on K_2O/Ba-MCM-41.

g, m(K_2O/Ba-MCM-41(K_2O 11 wt %): m(WCO) = 1:30, 430 °C for 110 min. Under the above conditions, the conversion of WCO and yield of bio-oil were 83.8% and 67.7%, respectively.

Stability of K_2O/Ba-MCM-41. Recycling of the catalyst is a crucial step as it can cut the cost of cracking production. The stability of the catalyst was studied, and the results were shown in Figure 3. The catalyst could be reused without further treatment after reaction. The conversion of WCO reached 82.1% even after four successive cycles of reuse. Moreover, after the fourth use, K_2O/Ba-MCM-41 still kept an excellent mesoporous structure (Figure S3, Supporting Information).[22] Thus, the catalyst can be recycled with negligible loss in activity.

CONCLUSION

The results presented in this work have shown that the pyrolysis of WCO can generate fuels that have similar chemical compositions to petroleum-based fuel by using K_2O/Ba-MCM-41 as a basic catalyst; it is possible to obtain cracking oils with low acid values and good cold flow properties such as the cold filter plugging point and freezing point. Importantly, the catalyst is easily separated from the production mixture and can be reused at least four times. Compared with other basic catalysts, such as Na_2CO_3 or K_2CO_3, K_2O/Ba-MCM-41 shows a high catalytic performance for cracking of WCO. Further studies of this pyrolysis reaction, such as using the other waste oil (rubber seed oil) as the raw material and different kinds of catalyst support, are needed and are currently under investigation by our research group.

Table 4. Effect of Reaction Conditions on Reaction Results*

m(cat)/ m(WCO)	temperature (°C)	time (min)	conversion %	yield of bio-oil (%)
1:50	400	150	75.8	58.9
1:40	400	150	76.5	60.3
1:30	400	150	77.8	62.7
1:20	400	150	77.3	61.3
1:10	400	150	77.1	59.2
1:30	410	150	78.8	63.1
1:30	420	150	82.3	65.6
1:30	430	150	83.8	67.5
1:30	440	150	83.9	67.1
1:30	450	150	84.0	65.7
1:30	430	90	77.3	64.1
1:30	430	100	81.1	66.0
1:30	430	110	83.8	67.7
1:30	430	120	83.9	67.7

*Reaction conditions: WCO 10 g, M(K_2O/Ba-MCM-41): M(WCO) = 1:50–10, 400–450 °C, 80–120 min.

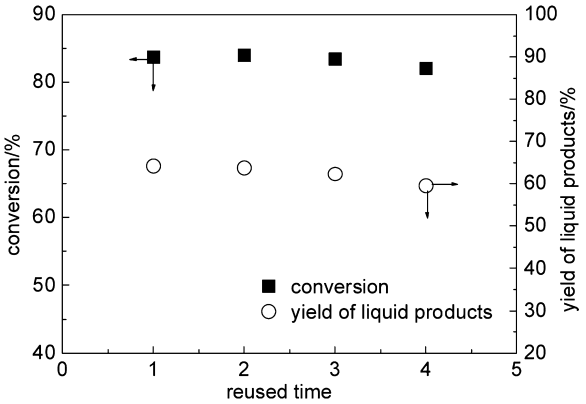

Figure 3. Stability of K_2O/Ba-MCM-41(WCO 10 g, M(catalysts): M(WCO) = 1:30, 430 °C, 110 min).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Structure of Ba-MCM-41, fresh K_2O/Ba-MCM-41, used K_2O/ Ba-MCM-41, and K_2O/Ba-MCM-41 from different concentrations of KNO_3 solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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