Pyrolysis of spill oils adsorbed on zeolites with product oils recycling

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Abstract

Experimentally, a feasibility study for adsorption and catalytic pyrolysis of spill oils on Cu/ZSM-5 for recycling of light oils has been conducted in the present work. The adsorption and pyrolysis of model compounds such as heptane, toluene, and diesel (to stimulate the spill oils) on Cu/ZSM-5 have been investigated on a continuous fixed-bed reactor. By component fitted X-ray absorption near edge structural (XANES) spectroscopy, catalytic active species such as metallic copper (Cu) (77–84%) and Cu2O (6–7%) are found in the channels of ZSM-5 during pyrolysis of heptane or toluene. Pyrolysis of diesel effected by Cu/ZSM-5 yields gas (C1–C5) (32%) and light oil (68%) that can be used as auxiliary fuels.

1. Introduction

It is estimated that in 2006, the total quantity of oil spilling was 13,000 tons approximately in the world (ITOPF, 2007). Oil spilling frequently occurring in the harbors and/or seashores may cause spreading, drifting, evaporation, dissolution, photolysis, biodegradation, and formation of water-oil emulsion. The superficial spill oils above the seawater surface usually insulated the oxygen transportation between air and seawater, and dramatically inhibited the photosynthesis of the algae. Generally, spilling oils may be treated by dispersion (to enhance decomposition of oils) or collection with skimmers.

Microporous zeolites such as ZSM-5 (Zeolite Socony Mobil-5) having high surface areas and superior catalytic activities are widely used in adsorption and catalytic degradation of organic compounds in liquid and gaseous phases. The unique shape selective catalysis capability of ZSM-5 makes it possible to directly control catalytic reaction paths with hydrocarbons (Weisz and Frilette, 1960). Iwamoto and coworkers found that copper exchanged ZSM-5 was very active in selective catalytic reduction of NO (Iwamoto et al., 1986).

Speciation data such as coordination number (CN), bond distance, and oxidation state for select elements in complex solids can be studied by X-ray absorption near edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies (Parsons et al., 2002). The molecular-scale data determined by XANES and EXAFS in supercritical water oxidation (Lin and Wang, 2000), solidification of fly ash as (Hsiao et al., 2001), mineralization of CCl4 (Chien et al., 2001), NO reduction (Huang et al., 2003), catalytic hydrogenation of CO2 (Liu et al., 2005) and photocatalysis of organic compounds (Hsiung et al., 2006) turn out to be very useful in revealing reaction paths and chemical structure of main active species involved in the catalysis processes. Thus, the main objective of the present work was to study the feasibility for adsorption and catalytic pyrolysis of spill oils on Cu/ZSM-5 with product oils recycling. In addition, chemical structure of copper active species involved in the catalysis process was also investigated by XANES and EXAFS.

2. Materials and methods

A Cu(NO3)2 (Fluka, 99%) solution was used in impregnation of 10 wt.% copper onto ZSM-5. The Cu/ZSM-5 catalyst calcined at 823 K for 4 h was characterized by X-ray powder diffraction (XRPD) (D8 Advance, Bruker) with CuKα (1.542 Å) radiation at the scanning rate of 3°/min. Nitrogen adsorption–desorption isotherms of the catalysts were determined at 77 K (Coulter SA3100, Beckman). Adsorption isotherms of heptane (MERCK, 99%) and toluene (MERCK, 99.9%) on Cu/ZSM-5 were determined by thermogravimetric analysis (SDT Q600, TA). The catalytic pyrolysis experiments were carried out on a continuous fixed-bed reactor. About 2 gm of the Cu/ZSM-5 catalyst were used in the catalytic pyrolysis of heptane, toluene, and diesel (Chinese Petroleum Corporation, Taiwan) that was used to stimulate the spill oils. The
pyrolysis product gases were analyzed by gas chromatography (GC-17A, Shimadzu).

XANES spectra of copper in the catalysts were recorded in the transmission mode on the Wiggler beamline (17C) at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The absorption beam energy was calibrated by the absorption edge of a copper foil at 8979 eV. The UXWAFS 3.0 program was used to analyze the XANES data (Stern et al., 1995). The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectra of the Cu/ZSM-5 catalysts after pre-edge baseline subtraction and normalization to the maximum post-edge intensity. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species in Cu/ZSM-5 (Fay et al., 1992). Semiquantitative analyses of the edge spectra of Cu/ZSM-5 were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the catalyst samples. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. CuO (MERCK, 99%), Cu2O (Aldrich, 97%), and Cu foil were used as model compounds for the linear combination fitting of the fresh and used catalysts. On the average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fitting results.

3. Results and discussion

The XRPD patterns of ZSM-5 and Cu/ZSM-5 are shown in Fig. 1. The peaks at 5–10° and 20–25° are suggestive of existence of the well-defined micro pores in ZSM-5. CuO on ZSM-5 is also observed at 35.6° and 38.7°. It is also found that mainly CuO is supported on ZSM-5 with little perturbation of the framework of ZSM-5 prior to pyrolysis.

Heptane and toluene were used to stimulate the aliphatic and cyclic hydrocarbons, respectively, in spill oils. Fig. 2 shows the adsorption isotherms of heptane and toluene on ZSM-5 (surface area = 380 m²/g) at 313 K for 200 min. It is clear that adsorption of heptane or toluene on ZSM-5 becomes saturated at the adsorption time of 50 min. Note that the maximum adsorption of heptane and toluene on ZSM-5 are about 100 and 75 mg/g ZSM-5, respectively. The straight channels of ZSM-5 have an elliptical cross section of 5.7–5.8 Å by 5.1–5.2 Å (Breck, 1974) which are interconnected by zigzag channels with a nearly circular cross section diameter of 5.4 Å and a channel length of 4.5–6.6 Å (Breck, 1974; Lee et al., 1992). Heptane with a kinetic diameter of much less than the openings of ZSM-5 can diffuse freely and be adsorbed on ZSM-5, while the toluene molecules are tight-fitted in the confined channels of ZSM-5.

Catalytic pyrolysis of heptane, toluene, and diesel on ZSM-5 and Cu/ZSM-5 was conducted on a continuous fixed-bed reactor. Fig. 3 shows the conversions of heptane, toluene, and diesel on ZSM-5 and Cu/ZSM-5 during pyrolysis at 573–823 K. As expected, in Fig. 3, pyrolysis of heptane in the channels of ZSM-5 occurs at 573–673 K with conversions of 15–50%. In the presence of copper active species, an enhanced pyrolysis by about twice is found. Note that the copper active species involved in the catalytic pyrolysis are Cu (84%) and Cu2O (6%) as observed by XANES (see Fig. 4b).
On the contrary, to have a similar conversion to heptane pyrolysis, the reaction temperatures for pyrolysis of toluene may be raised to 723–823 K. Cu and Cu2O may also be the main catalytic active species involved in the catalytic pyrolysis of toluene. The Cu and Cu2O on ZSM-5 are also the active species in the catalytic pyrolysis of toluene at 723–823 K. Nevertheless, about 11% of Cu on ZSM-5 involve in catalytic pyrolysis of diesel. Adsorption and catalytic pyrolysis of diesel on Cu/ZSM-5 yield gas (C1-C5; 32%) and light oil (68%) that can be utilized as auxiliary fuels.

## 4. Conclusions

In the presence of copper active species on ZSM-5, the catalytic pyrolysis of heptane can be enhanced by about twice. The XANES spectra of the Cu/ZSM-5 catalyst reveal that Cu (84%) and Cu2O (6%) are the active species involved in the catalytic pyrolysis of toluene. The Cu and Cu2O on ZSM-5 are also the active species in the catalytic pyrolysis of toluene at 723–823 K. Nevertheless, about 11% of Cu on ZSM-5 involve in catalytic pyrolysis of diesel. Adsorption and catalytic pyrolysis of diesel on Cu/ZSM-5 yield gas (C1-C5; 32%) and light oil (68%) that can be utilized as auxiliary fuels.

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### References


