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Preparation and Characterization of Fluid Cracking Catalysts Containing Pollucite

Commercial fluid cracking catalysts (FCC) contain faujasite zeolite dispersed in an inorganic oxide matrix (*1*). A structurally modified synthetic faujasite designated as USY is frequently used in commercial FCCs. Most matrices used in the manufacture of FCC catalysis consist of synthetic inorganic oxides (typically silica and alumina) used to impart attrition resistance to the catalyst and a natural component (typically clay) used as an inexpensive inert filler (*2*). A polymerized aluminum chlorohydroxide derived from the monomer, $Al_2(OH)_5Cl \cdot 2H_2O$, has been described as a matrix component imparting superior attrition resistance (*3*). This component is referred to as chlorohydrol subsequently in this work.

More recently, a new FCC catalyst containing pollucite (a cesium analcime) was described in the patent literature (*4*). The purpose of this work is to prepare and characterize fluid cracking catalyst compositions containing pollucite. ^{133}Cs NMR will be one of the characterization methods. The effect of incorporation of pollucite on the activity and selectivity of a fluid cracking catalyst were determined. A mechanism is proposed by which catalyst activity and selectivity are modified by pollucite. This mechanism is supported by characterization and catalytic data.

A method of preparing composite fluid cracking catalyst (FCC) involves mixing chlorohydrol with Kaolin clay and an aqueous slurry of USY zeolite (Grade Z-14 from the Grace Davison Division of W. R. Grace & Co.–Conn.), spray drying the mixture followed by calcination (*3*). A portion of the clay can be replaced by pollucite (*4*). Four pollucite containing catalysts where the input of pollucite was varied from 4 to 16 wt% were prepared. All the catalysts contained 35 wt% USY. The pollucite sample was obtained from the Tantalum Mining Corporation of Canada Limited. The USY sample contained 0.8% Na_2O, and had N_2 BET surface area of 771 m^2/g and unit cell size of 24.53 Å.

For the ^{133}Cs NMR work, the USY sample was ion exchanged using 0.1 *M* CsCl solution. The zeolite was then washed with deionized water and dried.

Mixtures of pollucite with either zeolite or the matrix components (Chlorohydrol and clay) were prepared for NMR characterization. These preparations involved intimately mixing an aqueous slurry of pollucite with the other ingredients, drying the mixture in a laboratory oven, followed by calcination using the same conditions as that used to prepare FCCs.

Chemical analysis of zeolites and composite catalysts for elements other than Cs were carried out using an inductive coupled plasma (ICP) analyzer. Cs was analyzed by X-ray fluorescence or atomic absorption. Unit cell size of zeolites and the zeolite component in catalysts were measured by X-ray diffraction using ASTM Method D-3942-80. Solid state ^{133}Cs MAS NMR spectra were obtained on a Bruker AM-400 NMR spectrometer (^{133}Cs frequency 54.483 MHz) using a Doty MAS probe. Typical experimental parameters used were: 90° pulse width, 1 sec relaxation delay, 5000 scans. Spinning speeds were 3–4 kHz. All spectra were processed using a 50-Hz expo-

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nential linebroadening. Chemical shifts were referenced using an external aqueous 0.1 *M* CsCl standard (0.0 ppm).

Hydrothermal pretreatment of FCCs prior to testing is customarily employed to simulate aging in a commercial unit (*5*). For this work, catalysts were pretreated for 4 h at 1089°K with 100% steam. Catalytic activity and selectivity were determined using a fixed-bed reactor and a method similar to that described by ASTM Method D 3907-80. A sour, imported heavy gas oil with 22.5 API gravity was used as the feedstock. Experiments were carried out at a reactor temperature of 800°K and catalyst residence time (*6*) of 30 sec. Liquid and gaseous products were analyzed with gas chromatograph (GC). Carbonaceous deposit on the catalyst was analyzed by Carbon Determinator WR-12 (Leco Corp., St. Joseph, MI). Weight hourly space velocity (WHSV) was varied to generate yield data for various products as a function of conversion. Research and motor octane numbers for the product gasoline were calculated for its GC composition using a method described by Cotterman and Plumlee (*7*). At least three runs with varying WHSV were carried out per catalyst. All the product yields were interpolated to a constant 65 wt% conversion and mass balanced. These interpolated yields were used to deduce the change in selectivity due to incorporation of pollucite.

Ion exchange with CsCl resulted in a zeolite containing 7.4 wt% Cs_2O. This zeolite was characterized by NMR along with composite catalysts containing pollucite. These composite catalysts contained from 0.74 to 3.2 wt% Cs_2O (Table 1). Replacement of a portion of clay with pollucite also resulted in an increase in Na content of the catalysts. Surface area and unit cell size of the fresh catalysts were not significantly altered by the addition of pollucite. As expected, unit cell size of all the catalysts declined due to hydrothermal treatment as a result of dealumination of the zeolite framework (*8*). However, catalysts containing pollucite exhibited higher unit cell size than the catalyst without pollucite. This indicates that the addition of pollucite reduced the degree of zeolite dealumination in the catalyst resulting from hydrothermal treatment.

The ^{133}Cs MAS NMR spectrum of a calcined pollucite sample consists of a single broad peak with a chemical shift of −10 ppm (Fig. 1a). Cesium-exchanged USY (calcined), on the other hand, exhibits a spectrum (Fig. 1c) containing two peaks with chemical shifts of −150 and −190 ppm. These peaks are likely to represent cesium cations binding to nonequivalent framework sites of USY. The ^{133}Cs MAS NMR spectrum of a calcined catalyst sample (mixture of pollucite, USY, and matrix components) is given in Fig. 1d. The two peaks in this spectrum are assigned to cesium cations in pollucite (−10 ppm) and

TABLE 1

Properties of Catalysts

Pollucite input into catalyst (wt%)	0	4	8	12	16
USY input (wt%)	35	35	35	35	35
wt% Na_2O	.37	.36	.40	.46	.50
wt% Cs_2O	.03	.74	1.6	2.4	3.2
wt% Al_2O_3	44	44	43	42	42
Unit cell size (*Å*)	24.50	24.50	24.49	24.52	24.51
BET surface area (m^2/g)	213	226	233	236	235
BET surface area after hydrothermal (1089°K) treat. (m^2/g)	126	131	131	121	114
Microactivity after hydrothermal (1089°K) treat.	59	64	67	68	69
Unit cell size after hydrothermal (1089°K) treat. (Å)	24.23	24.24	24.24	24.26	24.27

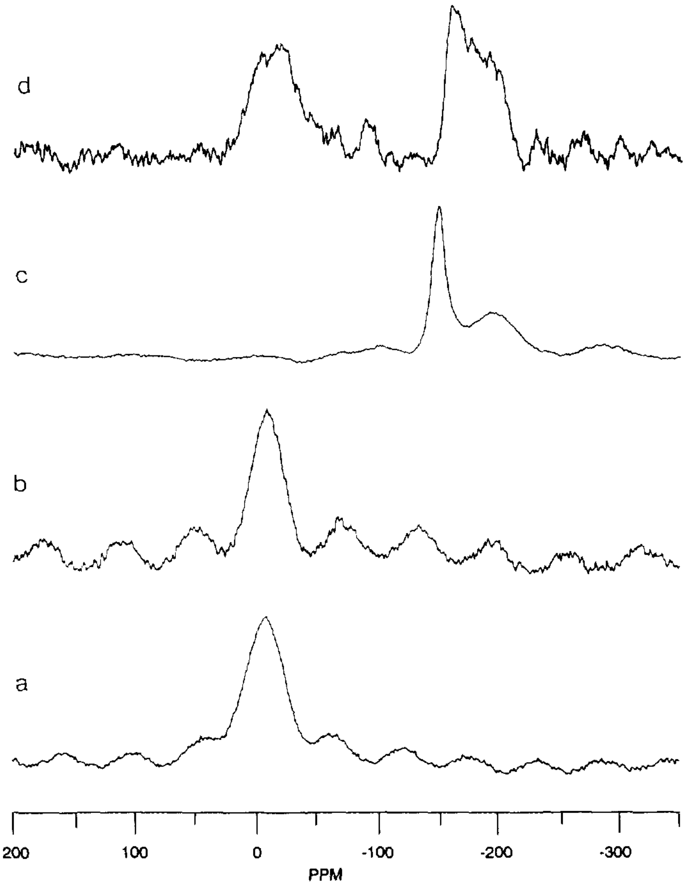

FIG. 1. ^{133}Cs MAS NMR spectra of calcined (a) pollucite, (b) pollucite in catalyst matrix (no USY), (c) cesium-exchanged USY zeolite and, (d) pollucite-containing catalyst.

USY (−180 ppm) environments based on their chemical shifts. This result suggests that cesium cations have migrated from the pollucite into the USY pores. The ^{133}Cs MAS NMR spectrum of a pollucite/matrix mixture (no USY), however, shows no evidence for cesium migration into the catalyst's matrix components (Fig. 1b).

Catalytic test results (Table 2) indicate that the addition of pollucite increased the cracking activity (measured after hydrothermal pretreatment). The increased activity is illustrated by the higher WHSV that can be used to achieve constant conversion of the gas oil. The addition of pollucite also affected selectivity. It resulted in a decrease in the selectivity for light hydrocarbons (C_1 to C_4) and an increase in gasoline selectivity. The octane number of the product gasoline was lowered with pollucite. The selectivity shifts became more pronounced at the higher concentration (12 to 16 wt%) of pollucite in the catalyst. The activity and selectivity shifts observed here are consistent with those reported by Pine *et al.* (*9*) for various cation-exchanged USY catalysts. The degree of cation exchange controls the degree of dealumination during hydrothermal pretreatment. This influences the unit cell size and acid site density of the pretreated catalyst which controls activity and selectivity (*9*). Catalysts with higher

TABLE 2

Interpolated, Mass Balanced Yields for Catalysts at 65 wt% Conversion

Pollucite input into catalyst (wt%)	0	4	8	12	16
Catalyst to oil ratio	4.6	4.2	3.7	3.6	3.4
WHSV, hr^{-1}	26	29	32	33	35
Yields (wt%)					
H_2	.1	.07	.05	.05	.05
$C_1 + C_2$	1.9	1.9	1.7	1.6	1.5
$C_3 + C_4$ olefins	10.2	10.2	9.3	8.8	8.3
Total $C_3 + C_4$	15.2	15.0	14.0	13.4	12.6
C_5^+ gasoline (C_5–216°C)	44.5	44.7	45.9	46.7	47.6
Light cycle oil (216–338°C)	23.0	23.0	23.0	23.0	23.0
Bottoms (338°C+)	12.0	12.0	12.0	12.0	12.0
Coke	2.8	2.8	2.8	2.8	2.8
Research octane number	90.4	90.2	89.6	88.8	88.7
Motor octane number	79.9	79.9	79.9	79.5	79.4

acid site density exhibit higher activity and selectivity for gasoline at the expense of lighter, C_4^--hydrocarbons. They also produce gasoline with lower octane number. Thus, addition of pollucite to an FCC catalyst modified activity and selectivity due to the migration of Cs from pollucite to zeolite. This migration reduced the degree of zeolite dealumination during the steam pretreatment and changed the acidity characteristics of the zeolite.

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R. KUMAR
E. F. RAKIEWICZ[1]
K. RAJAGOPALAN[2]

Grace Davison
W. R. Grace & Company–Connecticut
7379 Route 32
Columbia, Maryland 21044

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[1] Research Division.

[2] To whom correspondence should be addressed.