

# Chemical liquid deposition with polysiloxane of ZSM-5 and its effect on acidity and catalytic properties

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## Abstract

ZSM-5 acidity was modified by chemical liquid deposition of silica (SiO<sub>2</sub>-CLD), and the modification mechanism was investigated by pyrolysis gas chromatography-mass spectrometer (PGC-MS), absorbed pyridine infrared spectroscopy (Py-IR), temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), thermal gravity analysis (TGA), X-ray diffraction (XRD) and physical adsorption and probe-molecule reactions. In SiO<sub>2</sub>-CLD modification, the deposition process of polysiloxane modifier to silica over ZSM-5 is the acid-catalyzed degradation accompanying with the thermal pyrolysis, following oxidation at high temperature. Though the silanol hydroxyls of ZSM-5 disappear after the modification, most of the framework Al bridging hydroxyls and non-framework Al hydroxyls remain. Besides, the acidic amount of the modified ZSM-5 drops gradually with increasing extent of the modification, but the acidic strength distribution of the modified ZSM-5 is almost unchanged compared to parent ZSM-5. After the four-cycle modification, the conversion of 1,3,5-triisopropylbenzene (TIPB) in cracking over the modified ZSM-5 is reduced by 92%, so the external surface of the modified ZSM-5 may be regarded to be almost non-acidic due to coverage of deposition silica. Moreover, the modified ZSM-5 shows the high activity for cracking of cumene. High selectivity of *para*-xylene up to 96.2% is obtained in toluene disproportionation over the modified ZSM-5, compared to 24.3% selectivity of *para*-xylene over parent ZSM-5. Therefore, SiO<sub>2</sub>-CLD with polysiloxane is an ideal modification for obtaining the high shape-selective ZSM-5 catalyst.

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## 1. Introduction

In order to obtain the high shape-selectivity of the desiring reactant or product in catalytic reaction, it is necessary to passivate the acidic sites on the external surface of zeolite, as the external active sites are of no shape-selective without the space limitation of zeolite channels. A variety of modification methods have been adopted to improve

the catalytic selectivity of ZSM-5 for toluene disproportionation or alkylation reaction etc., such as impregnation of metallic or non-metallic compounds, chemical vapor deposition of silica (SiO<sub>2</sub>-CVD) and pre-coking [1–3]. Although organic base compounds with large molecular sizes could passivate the external acidic sites of zeolite to obtain the shape-selectivity; the shape-selectivity obtained by this modification is not stable under reaction conditions, especially at high reaction temperatures [4–6]. The supporting of metallic or non-metallic compounds over ZSM-5, such as H<sub>3</sub>PO<sub>4</sub>, CaO, MgO and Fe<sub>2</sub>O<sub>3</sub>, could eliminate the external acidic sites of zeolite, but greatly decreasing the acidic sites in channels [7–10]. The on-line pre-coking modification of zeolite is often difficult to be operated,

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and this modification has to be conducted again after regeneration of zeolite catalyst [11,12]. SiO<sub>2</sub>-CLD modification was adopted to prepare the commercial ZSM-5 catalyst for shape-selective disproportionation of toluene to *para*-xylene, replacing the pre-coking modification [13]. It was reported in Mobile's patents that in methylation of toluene or toluene disproportionation the high selectivity of *para*-xylene up to 90% may be reached by adjusting CVD or CLD conditions and selecting polysiloxane [14–16]. Compared to usual CVD in laboratory, CLD is more easily transferred to the large-scale industrial preparation.

The mechanism of SiO<sub>2</sub>-CVD modification with simple silica alkoxides, such as tetra-methyl-orthosilicate (TMOS) and tetra-ethyl-orthosilicate (TEOS), has been investigated by Niwa, etc [17–19]. It was considered that siloxane could react with the hydroxyls of zeolite by silylation, which resulted in silica deposition on the external surface and in channels of zeolites. However, with the respect to siliceous modifiers in SiO<sub>2</sub>-CLD, especially for the usual polysiloxane PDMS, it is still in need of study to clarify how polysiloxanes decompose – deposit, modify the acidity of zeolite and improve shape-selectivity. The previous works mainly investigated the relationship between acidity/pores and selectivity by means of different preparation methods [20,21]. It will be very meaningful to understand how modifier PDMS influence ZSM-5 acidity and selectivity in CLD modification by using new characterization, i.e., to clarify the change of modifier to deposited silica on ZSM-5.

In this work, the deposition of polysiloxane modifier to silica over ZSM-5 in SiO<sub>2</sub>-CLD was firstly investigated by pyrolysis gas chromatography-mass spectrometer (PGC-MS). Mechanism of modification for ZSM-5 acidity was studied by Py-IR, XRD, TGA, and NH<sub>3</sub>-TPD. The results show that the external acidic sites of ZSM-5 are almost eliminated after the four-cycle SiO<sub>2</sub>-CLD. The cracking reactions of TIPB and cumene show that SiO<sub>2</sub>-CLD with polysiloxane is an ideal modification to obtain the high shape-selective ZSM-5 catalyst.

## 2. Experimental

### 2.1. SiO<sub>2</sub>-CLD modification of ZSM-5

Polydimethylsiloxane (PDMS) as SiO<sub>2</sub>-CLD modifier was purchased from Dow Chemicals, and its molecular formula is as follows: CH<sub>3</sub>-(Si(CH<sub>3</sub>)<sub>2</sub>-O)<sub>*n*</sub>-CH<sub>3</sub>, with average molecular weight (MW) 2210.

Na-form ZSM-5 zeolite of Si/Al = 24 was synthesized according to the reported procedure [22]. The as-synthesized ZSM-5 was exchanged with NH<sub>4</sub>NO<sub>3</sub> solution at 363 K. NH<sub>4</sub>-form ZSM-5 was calcined at 823 K for 2 h to obtain H-form ZSM-5. Then, ZSM-5 was mixed with hexane solution of polysiloxane compound, i.e., PDMS at 10 wt% polysiloxane to ZSM-5 zeolite. After above mixture was stirred for 4 h at the room temperature, it was filtered and dried at 393 K. The above ZSM-5 supported with PDMS was calcined in air by heating it to 823 K at a rate

of 3 K/min and holding up at this temperature for 2 h. the one-cycle SiO<sub>2</sub>-CLD modification of ZSM-5 with polysiloxane was finished. After the same procedure as the above operation was repeated three time in, the four-cycle modified ZSM-5 by SiO<sub>2</sub>-CLD as a catalyst was obtained.

### 2.2. Characterization

The structure of ZSM-5 samples were characterized by using X-ray diffraction (XRD) (Rigaku D/max-RBX), diffractometer with Cu K $\alpha$  radiation (1.5417 Å), 30 mA and 40 kV in the high voltage source, scanning angle (2 theta) from 5 to 50.

ZSM-5 sample impregnated with polysiloxane was investigated by PGC-MS under the operation condition similar to that of the calcination treatment in SiO<sub>2</sub>-CLD. The sample was loaded in a micro-furnace of pyrolysis unit and heated up to 823 K. After the gaseous products from polysiloxane decomposition over the sample were on-line injected into GC-MS system, they were separated by high temperature Al-coated bonded capillary column (25 m  $\times$  0.25 mm i.d., 0.1  $\mu$ m, Alltech company USA) in a programmed temperature of 15 K/min from 373 K up to 653 K, and were identified by mass spectrometric detection.

Py-IR to characterize the acidic sites of ZSM-5 was conducted with a self-supported wafer of sample using Perkin-Elmer 2000 FT-IR spectrometry. The sample was first evacuated at 450 °C for 3 h and then cooled down to 120 °C. The adsorption of pyridine was performed at 120 °C. Pyridine adsorption infrared spectrum was, respectively, recorded at 200 °C.

NH<sub>3</sub>-TPD for the acidic amount and strength of ZSM-5 was determined using Altmira-100 Characterization System (Zeolton, USA). The sample was in situ dried at 550 °C for 1 h in the flow of helium and then cooled down to 120 °C. The adsorption of NH<sub>3</sub> was performed in the flow of 10 wt.% NH<sub>3</sub>/He at 120 °C, remaining for 45 min to excavate physical adsorption of ammonia on zeolite. The NH<sub>3</sub> desorption was conducted between 120 and 700 °C at a heating rate of 12 °C/min. TCD signal and temperature corresponding to NH<sub>3</sub> desorbed were recorded simultaneously. Weaker acidic sites and stronger acidic sites were divided and determined according to the jointing-point of two desorption peaks [23].

### 2.3. Catalytic test

The modification effect on acidity of ZSM-5 were also tested by probe-molecular reactions of 1,3,5-triisopropylbenzene (TIPB) cracking and cumene cracking, respectively, in the fixed bed reactor with on-line GC analysis according to the reported method [24]. The products were analyzed using on-line gas chromatography (Hp6890) with 50–0.32 mm i.d. FFAP capillary column and FID.

The catalytic reaction of toluene disproportionation was, respectively, carried out over the parent ZSM-5 and modified ZSM-5. The reaction was conducted in the

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