Supplementary Material

Effect of acidity of HZSM-5/MCM-41 hierarchical zeolite on its catalytic

performance in supercritical catalytic cracking of n-dodecane: Experiments and

mechanism

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Fig. S1. Schematic diagram of integrated apparatus for probe reaction of *n*-hexane

catalytic cracking and TPSR of *n*-dodecane.

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Fig. S2. Off-line analysis of the components of mixed gas sample collected at different temperature after ice-water bath gas washing during a typical *n*-dodecane

TPSR.



Fig. S3. Profiles of isothermal oxidation of commercial MCM-41 after supercritical

cracking of n-dodecane (460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00



mL/min) for 30 min.

Fig. S4. Profiles of isothermal oxidation of coked HZSM-5/MCM-41 hierarchical catalyst obtained from supercritical cracking of *n*-dodecane (460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00 mL/min) with TOS of (A) approximate 0 min and (B) 60

min.



Fig. S5. Comparison of the XRD patterns of the fresh HZSM-5/MCM-41 and coked HZSM-5/MCM-41 that prepared by supercritical catalytic cracking of *n*-dodecane

(460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00 mL/min) for approximate 0

min.

The supercritical catalytic cracking of *n*-dodecane with TOS \approx 0 min was carried out as follow: (1) 0.500 g HZSM-5/MCM-41 hierarchical catalyst was placed in the fixed-bed reactor; (2) the pressure of was increased to 4.0 MPa by compressed nitrogen; (3) the temperature was heated to 460 °C and then kept at 460 °C for 1 h with a nitrogen flow of 200 mL/min; (4) the nitrogen was turned off and then the feed pump was turn on (with a feed rate of 4.00 mL/min); (5) the feed pump was turned off immediately as the reactant contact with the catalyst bed, which was characterized by the sudden drop of the temperature of the catalyst bed; (6) the nitrogen was turned on again with a flow rate of 200 mL/min to sweep the *n*dodecane residing in the catalyst bed for 30 min, meanwhile the heating of the reactor was stopped. Finally, the coke properties and the crystalline structure of the coked catalyst were characterized by isothermal oxidation and XRD patterns, respectively.



Fig. S6 The evolution of the XRD patterns of coked HZSM-5/MCM-41 hierarchical catalysts obtained from low pressure catalytic cracking of *n*-dodecane (460 °C, partial pressure of *n*-dodecane \approx 33 kPa and WHSV=54 h⁻¹) with increasing TOS: (A) whole range of 2 theta; (B) $22^0 \le 2$ theta $\le 32^0$.



Fig. S7. Profiles of isothermal oxidation of coked HZSM-5/MCM-41 hierarchical catalysts obtained from low pressure catalytic cracking of *n*-dodecane (460 °C, partial pressure of *n*-dodecane \approx 33 kPa and WHSV=54 h⁻¹) with increasing TOS.



Fig. S8. The coke content of coked HZSM-5/MCM-41 hierarchical catalysts obtained from low pressure catalytic cracking of n-dodecane (460 °C, partial pressure of n-

dodecane \approx 33 kPa and WHSV=54 h⁻¹) versus TOS.

The low pressure catalytic cracking of *n*-dodecane was conducted in a fixed-bed reactor following the procedure described below: (1) 0.250 g HZSM-5/MCM-41 hierarchical catalyst (20-40 mesh) was place in a quartz tubular reactor (8 mm i.d.); (2) the temperature was heated to 460 °C with a nitrogen flow of 60 mL/min and then kept at 460 °C for 30 min; (3) the reactant of *n*-dodecane was fed into the reactor by a peristaltic pump at a speed of 5 rpm (0.3 mL/min) with continuous flow of nitrogen (60 mL/min); (4) the moment that the bed pressure suddenly increased was denoted as the zero time of TOS; (5) after the TOS reached the designed value (2, 20, 40 or 90 min) the peristaltic pump was stopped immediately while the nitrogen flow was continued for 15 min to sweep the reactant residing in the catalyst bed.



Fig. S9. Profiles of isothermal oxidation of coked parent HZSM-5 obtained from supercritical catalytic cracking of *n*-dodecane (460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00 mL/min) with TOS = 60 min.



Fig. S10. Profiles of temperature-programmed oxidation of the ion exchanged commercial MCM-41 (0.8 M NaCl) after the supercritical catalytic cracking of *n*dodecane (460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00 mL/min) for (A) 30 min and (B) 180 min.

Since no CO signals would appear during the isothermal oxidation of coked MCM-41 (Figure 9B), the method of temperature-programmed oxidation (TPO) was applied to characterize the coke deposited on ion exchanged commercial MCM-41 so as to provide more information on the coke. The TPO was operated as following: (1) 0.100 g coked catalyst was placed in the U-shaped quartz tube; (2) the carrier gas of air with a flow rate of 500 mL/min was turned on; (3) the sample was heated to 230 °C from 30 °C with a ramp rate of 20 °C/min and then kept at 230 °C for 40 min; (4) the temperature was increased from 230 °C to 800 °C with a ramp rate of 10 °C/min and then kept at 800 °C for 10 min. As shown in Figure S9, except for the evolution of the coke content that has been discussed in the manuscript, the low temperature oxidation peak was strengthened in the later stage of supercritical cracking, indicating that the way of coke deposition is really changed with increasing TOS for mesoporous MCM-41.



Fig. S11. Profiles of isothermal oxidation of coked NaHZSM-5/MCM-41_0.4M obtained from supercritical catalytic cracking of *n*-dodecane (460 °C, 4.0 MPa, 0.500 g catalyst and feed rate of 4.00 mL/min) with TOS = 60 min.

A theoretical analysis of the spatial distribution of the exogenous coke on mesopores.

From the point view of reaction engineering, the mesopores that disconnecting to the micropores are similar to the concept of "dead zone" in the catalyst particles, because the no obvious catalytic reaction happens except for the slowly exogenous coke deposition within these mesopores due to the low acid strength. In this quasidead zone, there is no driving force for the reaction medium that containing exogenous coke precursors to diffuse outward to the bulk of the reaction fluid. Therefore, the residence time of the exogenous coke precursors is infinite if the consumption of the coke precursors due to exogenous coke deposition is not considered. However, the situation in the mesopores connecting to micropores is not the same. If the inside micropores still have the catalytic activity, the coke precursors together with other products will diffuse outward from the inside micropores to the bulk reaction fluid through such mesopores. Although the concentration of the exogenous coke precursors is higher than that of the bulk reaction fluid, the residence time is limited by the catalytic reaction of the inside micropores. Therefore, whether exogenous coke deposits on the mesopores connecting or disconnecting to micropores depends on the relative intensity of the two factors of residence time and concentration effect of the exogenous coke deposition. Since the scale of the difference in residence time is greater than that in the concentration of the exogenous coke precursors, the exogenous coke is probably deposited in mesopores disconnecting to micropores.