



Short communication

Inductive effect of basic nitrogen compounds on coke formation during the catalytic cracking process

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ABSTRACT

This paper proposes a mechanism for the inductive effect of quinoline on coke formation during the catalytic cracking of *o*-xylene. Quinoline preferentially adsorbs on the acidic sites to induce coke formation and promote the conversion of *o*-xylene via electrophilic substitutions and hydrogen transfer reactions. The presence of naphthyl-quinolines and benzyl-quinolines in soluble coke identified by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry and the characterization of two types of nitrogen species in coke by XPS both confirm that the mechanism is reasonable. Basic nitrogen compounds poison the acidic sites of catalysts and induce the coke formation from aromatics.

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1. Introduction

Fluid catalytic cracking (FCC) is one of the most important processes in petroleum refining to produce transportation fuels including gasoline, light cycle oil, and liquefied petroleum gas (LPG) [1,2]. Coke deposited on catalysts is an undesirable by-product and the principal cause of catalyst deactivation [3]. The coke is mainly composed of highly condensed aromatic compounds, which temporarily deactivate the active sites of the catalyst by poisoning, pore blockage or both [4]. During the FCC process, coke formation involves several consecutive reactions. Alkanes undergo cracking to produce olefins, which proceed via the oligomerization, cyclization, and hydrogen transfer reactions to produce naphthenes. The naphthenes proceed via other hydrogen transfer reactions and dehydrogenations to form aromatics, and then the olefins, naphthenes, and aromatics undergo inter- and intra-molecular hydrogen transfer reactions, polymerizations, and dehydrogenations to produce coke [3,5]. Therefore, hydrocarbons of the FCC feedstock including alkanes, naphthenes, and aromatics can all act as precursors to form coke, while the formation of an initial aromatic ring is essential in the coke-forming reactions.

In addition to hydrocarbons, the FCC feedstock contains non-negligible amounts of sulfur-, oxygen-, and nitrogen-containing compounds. The damaging effects of nitrogen compounds, especially basic nitrogen compounds, on acidic catalysts have been proven to be another important cause of catalyst deactivation for several decades [6–11]. In

recent years, due to the increasing level of nitrogen content in the FCC feedstocks, the damaging effects of nitrogen compounds toward catalysts have become a very serious problem [12–20]. Previous works have argued that the nitrogen compounds poisoned the acidic sites and that this poisoning effect increased with the addition of rings in the nitrogen compounds. For example, the damaging effect increased according to the series of pyridine, quinoline, and acridine [6–8]. Our research group obtained the same results [21]. When we added the same proportion (0.2 wt.% of nitrogen in the feedstock) of pyridine, quinoline, and acridine into vacuum gas oil, the conversion increasingly decreased more sharply. In general, a low conversion indicated a low coke yield from hydrocarbons. However, we found that the coke yield of hydrocarbons (subtracted nitrogen compound injection from total coke yield) increased in the presence of nitrogen compounds, which indicated that nitrogen compounds probably induced the coke formation of hydrocarbons. Previous works [2,22–25] have identified the nature of nitrogen species in coke and stated that the electrophilic substitution of quinoline with hydrocarbons could be performed over FCC catalysts. The presence of quaternary-nitrogen identified by ref. [25] is a probable evidence to support the inductive effect of nitrogen compounds on coke formation. However, these works paid attention to the nature of nitrogen species and the transformation of these nitrogen species to N₂ and NO_x during oxidative regeneration. These works didn't involve the effects of nitrogen compounds on the coke formation of hydrocarbons.

In this paper, the inductive effect of basic nitrogen compounds on coke formation during the catalytic cracking process was investigated. The selected hydrocarbon coke precursor was *o*-xylene, as the formation of an initial aromatic ring is essential in coke-forming reactions. The selected basic nitrogen compounds were pyridine, quinoline, and

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acridine, which could be representative of the typical nitrogen compounds in the FCC feedstocks [26]. Their catalytic cracking performance and coke formation over a commercial equilibrium catalyst were discussed. We believe that the results obtained here could be of interest in the study of the catalyst deactivation mechanism and could be valuable in understanding the damaging effects of nitrogen compounds on the FCC catalyst.

2. Experimental section

2.1. Feedstocks and catalyst

Analytical reagent grade (> 99%) pyridine, quinoline, acridine (> 98%), and *o*-xylene (Aldrich Chemicals) were used as additives and precursors for the coke-forming experiments. A commercial equilibrium FCC catalyst LVR-60R, with a main active component of USY zeolite, was employed, and it was supplied by the Changqing Petrochemical Co. of CNPC. Its main physicochemical properties are listed in Table 1.

2.2. Catalytic cracking experiments

Catalytic cracking experiments were performed in a fixed-bed micro-reactor, and its details have been described elsewhere [27]. The reaction conditions were a temperature of 500 °C, a catalyst to oil ratio of 5, and a WHSV of 6 h⁻¹. The *o*-xylene or a mixture of *o*-xylene with pyridine, quinoline, or acridine (0.2 wt.% of nitrogen in the reactant) was introduced into the reactor using a syringe pump. The reactant flow was 30 g/h, and the feeding time was 120 s. After catalytic cracking, the gas products were analyzed by a Bruker 450 GC gas chromatograph to determine the volume percentage of H₂ and N₂ as well as the mass content of C₁–C₆ hydrocarbons. The liquid products were measured by PIONA analysis on a Varian CP-3800 GC. Elemental analyses (C and N) of coked catalysts were carried out on a Vario EL III CHNS/O elemental analyzer (Elementar Co., Ltd., Germany). The conversion is defined as the total of the yields of dry gas, LPG, C₅⁺ aliphatic hydrocarbons, and coke. It can be calculated by

$$\text{conversion} = Y_{\text{dry gas}} + Y_{\text{LPG}} + Y_{\text{C}_5^+ \text{ aliphatic hydrocarbons}} + Y_{\text{coke}} \quad (1)$$

where *y* is the yield of products.

2.3. Coked catalyst characterization

To separate the coke species from the inorganic catalyst matrix, the coked catalysts were submitted to a three-step procedure [2]. First, approximately 3 g of coked catalyst was dissolved in a HF (40%) solution at room temperature. Next, the solution was neutralized with NaHCO₃. Finally, a three-step extraction with CH₂Cl₂ was carried out in a Soxhlet extractor. The nitrogen species in soluble coke were ionized by electrospray ionization (ESI) and analyzed by a Bruker Apex-Ultra Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) instrument equipped with a 9.4 T superconducting

Table 1
Properties of the commercial FCC catalyst LVR-60R.

Catalyst	LVR-60R
Al ₂ O ₃ content (wt.%)	48.2
Bulk density (g/cm ³)	0.730
Attrition index (wt.%)	2.1
Specific surface area (m ² /g)	153
Average pore diameter (μm)	76
Particle size distribution (wt.%)	
0–40 μm	12.0
40–149 μm	83.6

magnet at the China University of Petroleum (Beijing, China). The details of the analysis methods have been reported elsewhere [20,28]. The insoluble coke was recovered by filtration.

The coked catalyst was characterized (N1s) by XPS (PHI-5000 Versaprobe). To distinguish the types of nitrogen specie present in coke, N1s envelopes were subjected to a deconvolution procedure using a minimal number of peaks and varying the FWHMs, positions and intensities of the peaks to result in the best NLLS fit ($\chi^2 = 0.98$). A mixture of Gaussian (80%) and Lorentzian (20%) functions was used [25].

3. Results and discussion

3.1. Effects of nitrogen compounds on the catalytic cracking performance of *o*-xylene

As shown in Table 2, during the catalytic cracking process, *o*-xylene mainly undergoes isomerization and disproportionation to produce other aromatic hydrocarbons due to the stability of the benzene ring. A few of these aromatic hydrocarbons perform ring opening and cracking to generate aliphatic hydrocarbons or undergo polymerizations and dehydrogenations to form coke. The conversion of *o*-xylene decreases in the presence of pyridine. The yields of dry gas, LPG and C₅⁺ aliphatic hydrocarbons all decrease and the coke yield increases. This coke yield includes poly-aromatics formed from hydrocarbons and pyridine adsorbed and deposited on the catalyst. The former (marked as coke-I) also declines as the coke yield increases with the conversion decreasing. These results are in agreement with those of previous works. Pyridine reversibly adsorbs onto the acidic sites of the catalyst, resulting in a decrease in active sites, which leads to decreases in the yields of all of the products. Pyridine also can act as a coke precursor due to its size and aromatic nature, resulting in an increase in the total coke yield. According to this poisoning mechanism of basic nitrogen compounds, the conversions of *o*-xylene should decrease sharply in the presence of quinoline and acridine. They can more preferentially adsorb onto the acidic sites and desorb less easily than pyridine, thus occupying more active sites. As shown in Table 2, however, the conversions show marked increases, and the yields of dry gas, LPG, and C₅⁺ aliphatic hydrocarbons all increase. The obvious increases in the HTC (it indicates the coefficient of hydrogen transfer, which is defined as the volume ratio of butanes to butenes) values demonstrate that the hydrogen transfer reaction performs more actively. These results indicate that more *o*-xylene can be saturated by hydrogen transfer reactions and proceed

Table 2
Catalytic cracking performance of *o*-xylene with and without different nitrogen compounds.

Additives ^a	None	Pyridine	Quinoline	Acridine
Conversion ^b , wt.%	7.81	6.54	12.58	18.50
Yield, wt.%				
Dry gas	1.18	1.04	1.75	2.11
Liquid petroleum gas	2.49	1.85	4.29	6.65
Aliphatic hydrocarbons (C ₅ ⁺)	3.22	2.52	4.39	6.71
Aromatic hydrocarbons	92.19	93.46	87.42	81.50
Coke	0.92	1.13	2.15	3.03
Coke-I ^c	0.92	0.62	1.14	1.47
H ₂	0.01	0.01	0.05	0.13
HTC ^d	0.36	0.34	0.65	0.62
N _{liquid product} /N _{coke} ^e	–	54/46	46/54	39/61

^a Concentrations of the additives are 0.2 wt.% nitrogen.

^b The conversion is defined as the total of the yields of dry gas, LPG, C₅⁺ aliphatic hydrocarbons, and coke.

^c The yield of coke-I does not include nitrogen compounds adsorbed and deposited on the catalyst.

^d HTC indicates the coefficient of hydrogen transfer, which is defined as the volume ratio of butanes to butenes.

^e N_{liquid product}/N_{coke} means the relative proportion of nitrogen in liquid product and coke.

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