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Roles of NO and O_2 on coke deposition and removal over Cu-ZSM-5

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Abstract

Toluene and propene are used as model hydrocarbon gases for producing coke over Cu-ZSM-5. Temperature programmed oxidation technique is adapted to investigate roles of NO and O_2 on coke deposition and removal over Cu-ZSM-5 catalyst. It is found that when a gas mixture of NO and O_2 is added during hydrocarbon exposure, the carbonaceous structure is not changed but the deposition rate is dramatically increased. It is suggested that the presence of NO + O_2 accelerates hydrocarbon deposition or that coke may be formed in another route involving SCR. In addition, N_2 is detected during TPO by O_2 of this exposed Cu-ZSM-5. This indicates that nitrogen compounds have to be a part of carbonaceous deposits or they may adsorb on the deposits on the zeolite. By using XRD and ex situ FT-IR, it is found that the structure of coke is polyaromatic, not graphite-like form. It is also found that gasification reactivity of the carbonaceous deposits depends on the oxidizing gas (O_2, NO, NO + O_2) with respect to both composition and concentration. However, the rate of the gasification at each maximum temperature is about similar, independent on the oxidizing agent. Furthermore, N_2 peaks appear to coincide with CO_2 peaks. Therefore, in the presence of NO, CO_2 appears to be formed preferably by NO reduction rather than coke combustion. NO seems to be more reactive for oxidizing of carbonaceous deposits rather than O_2. Certainly, NO plus O_2 in the TPO oxidizing gas accelerates coke removal.

Keywords: Cu-ZSM-5; Coke deposition; Coke removal; TPO; NO and O_2

1. Introduction

Coke deposition is an important deactivation mode in the hydrocarbon conversion processes [1–5]. Attempts to understand the behaviors of coke deposition have widely been made. The chemical nature of the carbon deposits has been concluded to depend very much on how they are formed, the conditions of temperature and pressure, the age of the catalyst and the chemical nature of the feed and products formed [6–11]. Most researchers have emphasized coke formation in only reducing atmospheres, e.g., dehydrogenation, cracking, reforming, etc. However, coke deposition can also take place even in oxidizing atmospheres. Additionally, some oxidizing agents such as NO and O_2 can be contaminated in the feedstock. Thus, it is also important to study the coke deposition in the oxidizing atmospheres.

Coke is preferentially formed on the strong acid sites such as zeolite surface, which is widely used in many reactions, e.g., aromatization [8], cracking [12]. Moreover, a series of zeolite-based catalysts has been recognized for being NO_x abatement catalysts, especially, Cu-ZSM-5 [13–28]. Understanding the coke formation on Cu-ZSM-5 in the oxidizing atmosphere would therefore be an important step in studying the catalyst deactivation by coking of this zeolite. The focus of our objective is on the effects of oxidizing agents on the coke deposition (and also removal) on Cu-ZSM-5. This is accomplished by carrying out the coke gasification reactivity on Cu-ZSM-5 using NO and O_2 as oxidizing agents. The detailed mechanistic knowledge on coke formation associated with the structural characteristic of the deposits present on the coked catalysts is accomplished by employing TPO, FT-IR and X-ray diffraction (XRD) techniques. The results of this study are important for

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establishing an effective methodology for the reduction of coke formation on Cu-ZSM-5 and other metal-exchanged ZSM-5-based catalysts for the reaction involving oxidizing atmosphere.

2. Experimental

The Cu-ZSM-5 catalysts were prepared by ion-exchanging Na-ZSM-5 with 0.01 M $Cu(NO_3)_2{\cdot}3H_2O$ using about 250 ml solution for 5 g of catalyst. Then, 10% NH_4OH solution was dropped into the mixture to get the appropriate pH level (pH 9–11). The ion-exchange was performed for 24 h at ambient temperature under continuous stirring. After these treatments the catalyst was washed with deionized water about three to five times and dried at 110 °C for at least 3 h. Then, the Cu-ZSM-5 catalyst was calcined in air at 540 °C for 3.5 h. The total copper loading in Cu-ZSM-5 was about 2 wt.%. All catalyst powders were palletized and then cut with a knife into 8–16 mesh sections for using in the experiments.

The apparatus used for catalyst pretreatment, reaction and temperature programmed oxidation consisted of a conventional microreactor made from quartz tube with 0.6 cm inside diameter. The pretreatment and reactant gases were fed into the reactor by means of gas cylinders equipped with pressure regulators, needle valves for flow adjustment of the feed gas and a saturator for introducing toluene. The reactor was mounted in an electric furnace, which supplied the required heating with a temperature controller capable of maintaining temperature from ambient to 800 °C. Analyses employed a SHIMADZU GC-8ATP with a MS-5A column for O_2 and N_2 detection whereas C_3H_6 and CO_2 were analyzed by a SHIMADZU GC-8AIT with a Porapak-QS column.

Prior to use, the catalyst pretreatment was carried out under He atmosphere at 500 °C for 1 h. In the first approach, coke formation on Cu-ZSM-5 with different adsorbed species (HC only, HC + NO and HC + NO + O_2) was investigated. Propene and toluene are model hydrocarbons used in this study. Exposure in terms of carbon moles was made identical so that the propene flow rate was 1/3 of toluene flow.

A specified reactant gas was introduced into the catalyst bed at 400 °C with a GHSV of approximately 2000 h^{-1} for 20 min. After exposure, the catalyst samples were analyzed by temperature programmed oxidation (TPO) using either only O_2 or NO + O_2 as the oxidizing gas. TPO was performed by passing 100 ml/min of an oxidizing gas mixture through the micro reactor while slowly heating from

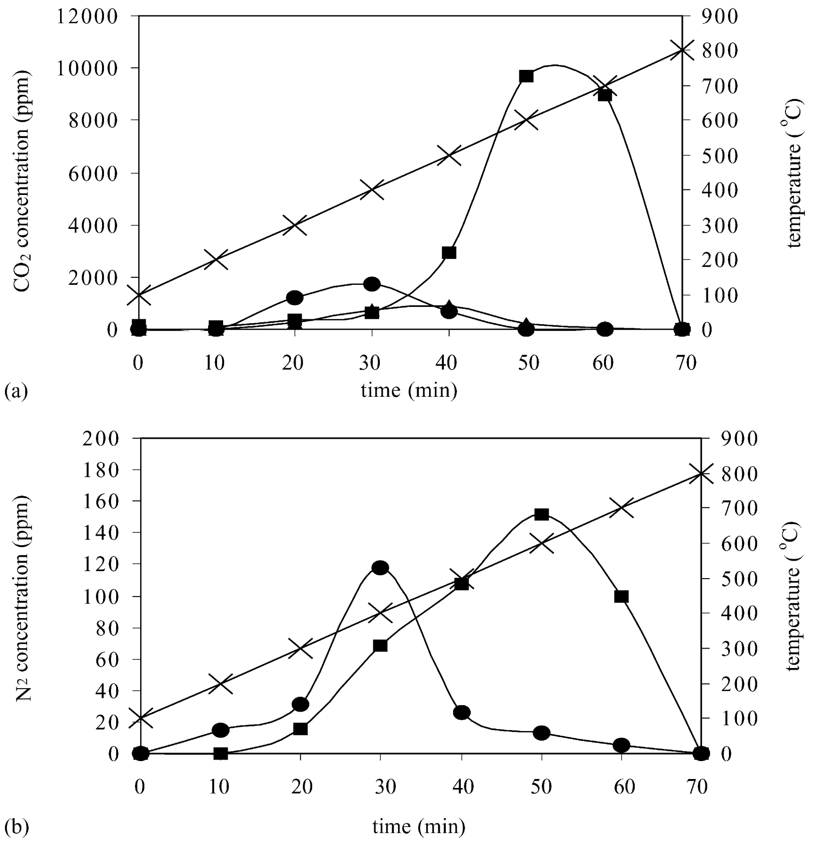

Fig. 1. (a) CO_2 and (b) N_2 concentration from reactor outlet of temperature programmed oxidation of carbonaceous deposits produced on Cu-ZSM-5 catalyst with various adsorbed gas mixtures: (▲) C_3H_6; (●) C_3H_6 + 1000 ppm NO; (■) C_3H_6 + 1000 ppm NO + 10% O_2; (×) temperature.

50 to 800 °C at a rate of 10 °C/min. The effluent gas was monitored every 10 min.

In the second part, attempts to investigate the coke removal behavior were made. Carbon deposits were produced at 400 °C for 20 min only by propene or toluene. Coke removal was conducted by TPO with O_2, NO or NO + O_2 at different concentrations; 1000 ppm NO/He, 1000 ppm O_2/He, 1000 ppm NO + 1000 ppm O_2/He, 1000 ppm NO + 1% O_2/He and 1% O_2/He.

All gases used in this study; 1% NO in He, 3% propene in He, 1% O_2 in He, 99.999% O_2 and 99.999% He, were supplied by Thai Industrial Gas (TIG). The 99.5% toluene was provided by Carlo Erba Reagenti.

The structural properties of carbonaceous deposits were characterized by an ex situ IR technique using a Nicolet Impact 400 analyzer equipped with a DTGS detector. IR experiment was performed ex situ after coke was generated on the catalyst surface at 400 °C for 20 min under different atmosphere (C_3H_6 or C_3H_6 + NO + O_2). Inert gas (He) was purged for 10 min at the same temperature in order to get rid of physisorbed species. After cooling down to ambient temperature, the catalyst was taken out of the reactor for IR measurement. The catalyst was ground into powder, which would be mixed with KBr to make a self-supporting disk and put into the IR cell where transmittion was undertaken between 400 and 4000 cm^{-1}. The crystal characteristics of carbon deposits were analyzed by X-ray diffraction using a SIEMENS SRD D500 X-ray refractometer with Ni-filterd Cu Kα radiation.

3. Results and discussion

3.1. Influence of dosing gas mixtures on coke deposition

The production of carbonaceous deposits by the adsorbed gas mixtures was studied in three systems. In addition to the hydrocarbon (propene or toluene), NO or a mixture of NO + O_2 was introduced into the catalysts to produce carbon deposits. Fig. 1(a) illustrates the TPO spectra observed over the coked Cu-ZSM-5 catalysts after being adsorbed with C_3H_6, C_3H_6 + NO and C_3H_6 + NO + O_2. It is shown that higher amounts of carbon deposits are formed after a gas mixture of NO + O_2 was also introduced on the catalysts. Particularly, the amount of carbonaceous deposits from the C_3H_6 + NO + O_2 system was approximately 10 times higher than the other two systems. Considering the amount of N_2 detected during the TPO experiment in Fig. 1(b), N_2 is

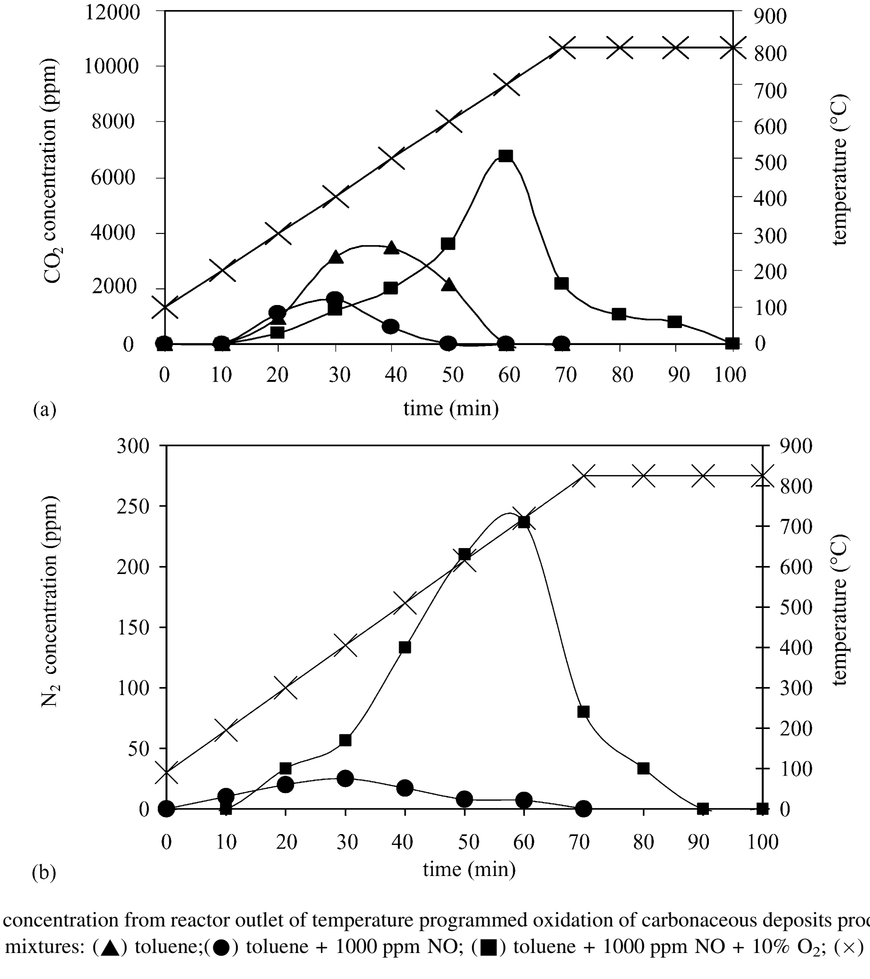

Fig. 2. (a) CO_2 and (b) N_2 concentration from reactor outlet of temperature programmed oxidation of carbonaceous deposits produced on Cu-ZSM-5 catalyst with various adsorbed gas mixtures: (▲) toluene;(●) toluene + 1000 ppm NO; (■) toluene + 1000 ppm NO + 10% O_2; (×) temperature.

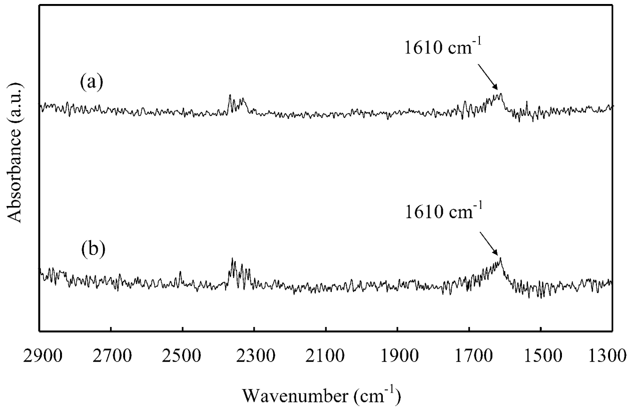

Fig. 3. IR spectra of Cu-ZSM-5 catalyst after adsorption by (a) C_3H_6; (b) C_3H_6 + NO + O_2.

emerged both in the C_3H_6 + NO and C_3H_6 + NO + O_2 systems. An analogous result is observed when the hydrocarbon reactant was changed from propene to toluene following in Fig. 2(a) and (b). However, the amount of carbon deposits on the catalysts from toluene + NO + O_2 was higher than toluene + NO and toluene only about 4 times. Two plausible explanations for higher amount of coke formed in the system where NO + O_2 are present in the coke deposition may be proposed here: (i) the alteration of coke propagation occurs with the presence of NO and O_2 or (ii) the pathway of coke formation is changed to NO reduction mechanism in the SCR of NO [29,30]. The structure of coke remaining on the catalysts was studied by means of the corresponding IR bands. Fig. 3 shows the IR spectra of the coked catalysts produced by C_3H_6 and C_3H_6 + NO + O_2. A feature at 1610 cm^{-1}, which corresponds to stretching mode of aromatic system, was detected in both catalysts. There was no IR band observed between 3010 and 3100 cm^{-1} where aromatic rings might be presented (not shown here). It is possible that the presence of a broad band of OH-stretching mode of adsorbed water was seen between 2900 and 3500 cm^{-1} [31] may conceal the aromatic signal. No IR adsorption features corresponding to aliphatic hydrocarbons, which lie between 2970 and 2850 cm^{-1} were observed from the coked catalysts [31]. It is also remarkable that differences in the results from IR and TPO may be possible

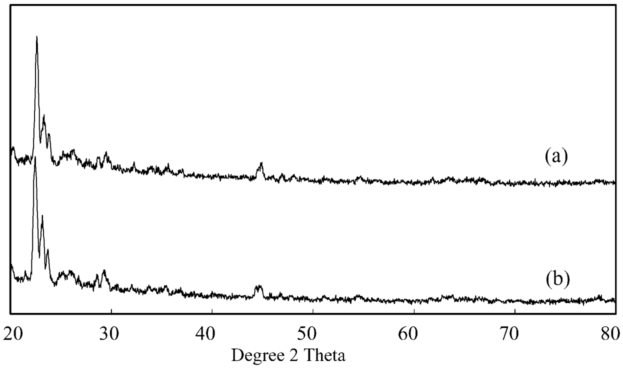

Fig. 5. XRD spectra of carbonaceous deposits sample on Cu-ZSM-5 catalyst after adsorption by (a) toluene; (b) toluene (3 mol% of C) + 1000 ppm NO + 10% O_2/He.

Table 1
The amount of carbonaceous deposits on Cu-ZSM-5 catalysts with various oxidizing gases

The oxidizing gas	The amount of carbon on catalyst (wt.%)	
	C_3H_6	Toluene
1000 ppm NO/He	0.4	2.08
1000 ppm O_2/He	0.45	2.05
1% O_2/He	0.52	2.15
1000 ppm NO + 1% O_2/He	0.47	2.12
1000 ppm NO + 1000 ppm O_2/He	0.44	2.10

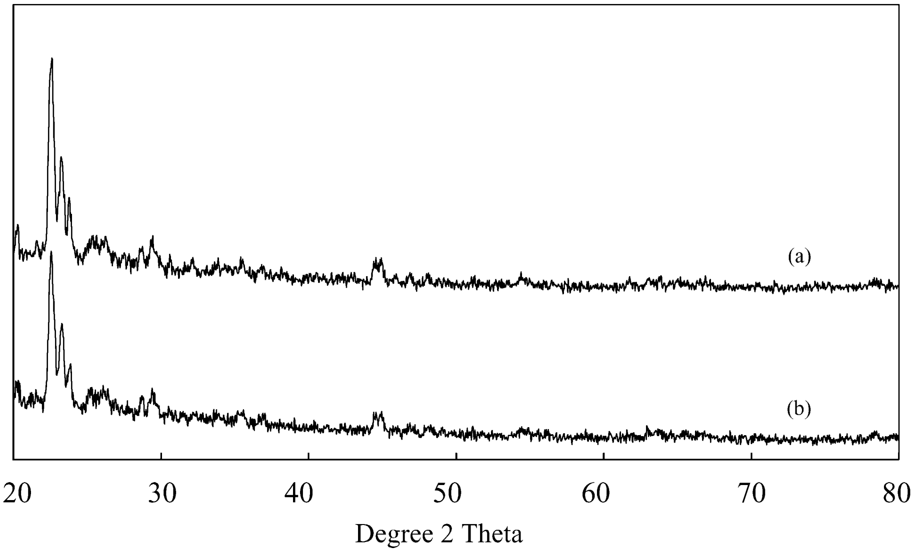

Fig. 4. XRD spectra of carbonaceous deposits sample on Cu-ZSM-5 catalyst after adsorption by (a) C_3H_6; (b) C_3H_6 (3 mol% of C) + 1000 ppm NO + 10% O_2/He.

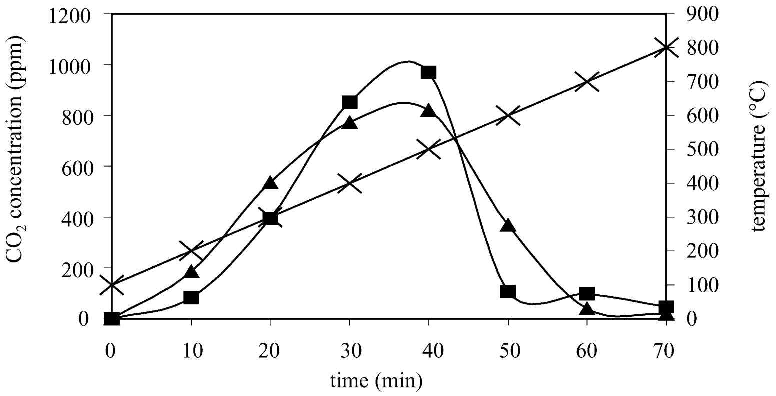

Fig. 6. TPO patterns of Cu-ZSM-5 catalyst with various reactants for the same amount of carbon ($C_3H_6C_3H_6$ + NO + O_2).

because those tools are focusing on different images. IR gives us the information of coke structure while the amounts of coke formation as well as the oxidation characteristic were obtained by TPO. For example, aromatic coke on the metal and the support would be demonstrated at the same frequency in IR experiment. However, when we study the two systems from TPO, different maxima would be certainly observed.

The formation of graphite-like coke was checked by XRD as seen in Figs. 4 and 5. No significant peak assignable to graphite was observed on the catalysts after exposure either to propene or toluene. Presence of NO and O_2 made no difference. Hence, graphitic domains are apparently not produced in the carbonaceous deposits in all systems. Therefore, it seems likely that carbonaceous deposits on the catalysts are aromatic species.

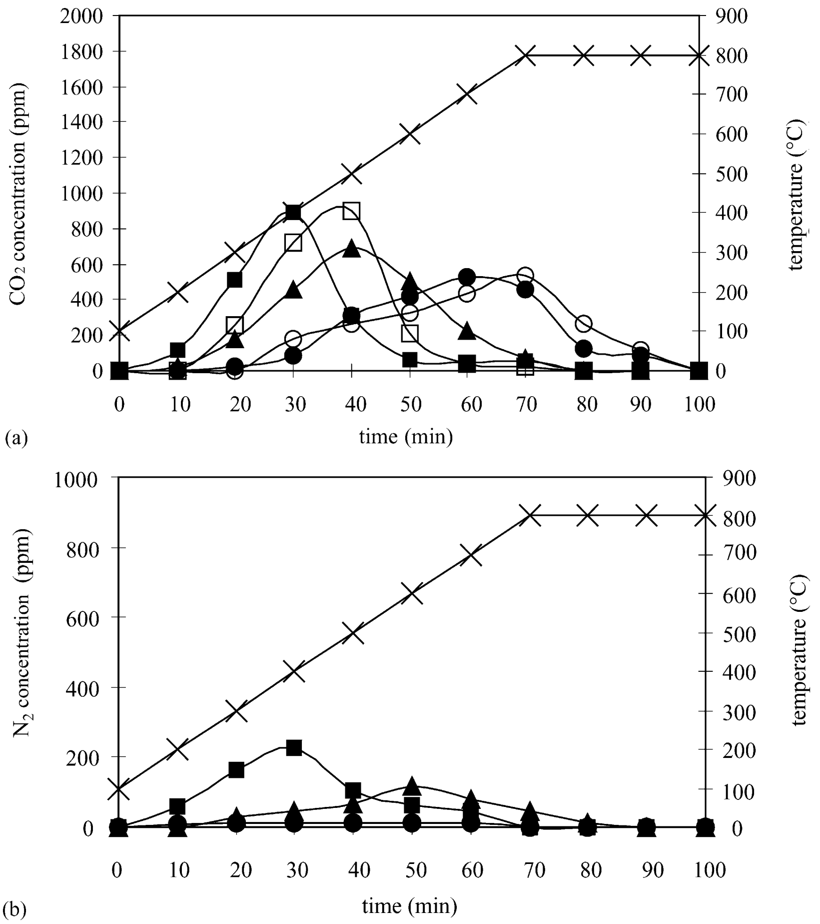

Fig. 7. (a) CO_2 and (b) N_2 released during TPO on Cu-ZSM-5 after exposure to propene at 400 °C for 20 min using various oxidizing mixed gases as follows: (○) 1000 ppm O_2; (●) 1000 ppm NO; (▲) 1000 ppm NO + 1000 ppm O_2; (■) 1000 ppm NO + 1% O_2; (□) 1% O_2; (×) temperature.

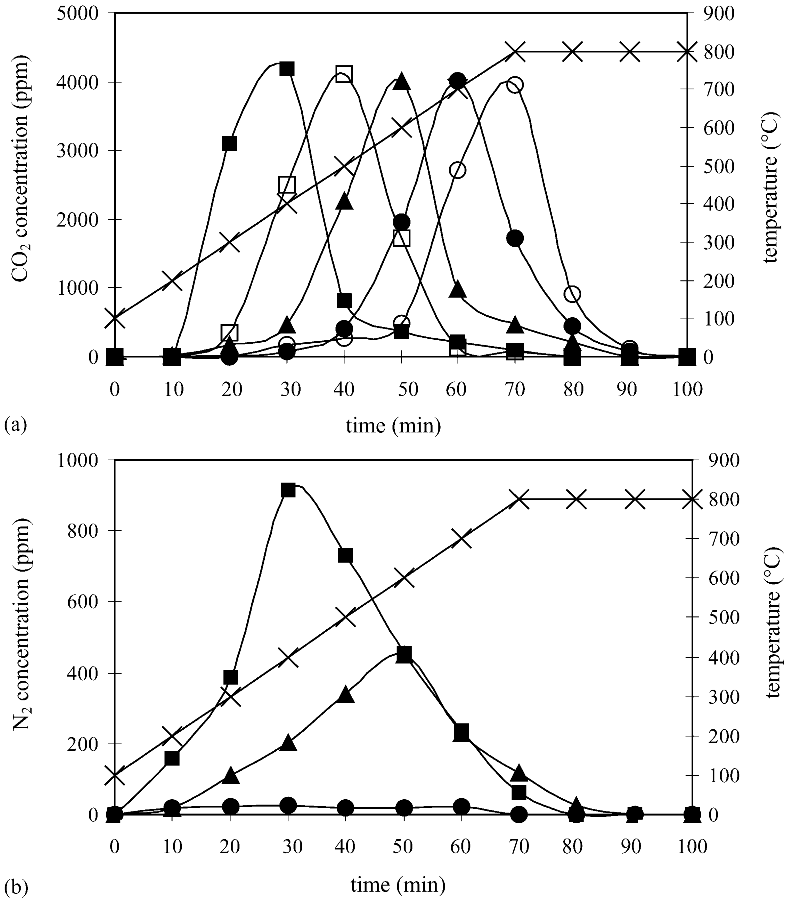

Fig. 8. (a) CO_2 and (b) N_2 released during TPO on Cu-ZSM-5 after exposure to toluene at 400 °C for 20 min using various oxidizing mixed gases as follows: (○) 1000 ppm O_2; (●) 1000 ppm NO; (▲) 1000 ppm NO + 1000 ppm O_2; (■) 1000 ppm NO + 1% O_2; (□) 1% O_2; (×) temperature.

The effect of duration of reactant exposure on the coke formation and reactivity is also investigated. TPO spectra of Cu-ZSM-5 being exposed to C_3H_6 for 90 min and C_3H_6 + NO + O_2 for 2 min, see Fig. 6, show the same peak temperature at 480 °C with the same pattern. Also, the amount of carbonaceous deposits on both catalysts is quite similar (ca. 0.6%). It is suggested that the time to produce coke is lessened by the presence of NO and O_2.

3.2. *Effect of oxidant on the coke removal*

Dependence of removal reactivity of carbonaceous deposits on the oxidizing gas with respect to both composition and concentration was also explored. Cu-ZSM-5 was exposed to hydrocarbon gas at 400 °C for 20 min, and then the coked catalysts were oxidized by NO, O_2 or NO + O_2 in various concentrations as illustrated in Table 1, where the amount of carbonaceous deposits was also compiled. The amount of carbonaceous deposits over the catalysts adsorbed before being oxidized is about the same (both for propene and toluene). Characteristics of coke on both catalysts were investigated by TPO using various oxidizing gases and concentrations as illustrated in Figs. 7 and 8. Resemble TPO patterns are exhibited when only one oxidizing gas is used (NO or O_2). However, the lower peak temperature is detected in the case of NO. Considering the spectra where two oxidizing agents are present, the lower maximum temperature is observed when the higher O_2 concentration is used. Therefore, the order of the efficiency on the coke removal on both hydrocarbons was 1000 ppm NO + 1% O_2/He > 1% O_2/He > 1000 ppm NO + 1000 ppm O_2/He > 1000 ppm NO/He > 1000 ppm O_2/He, respectively.

N_2 evolution curves in Figs. 7(b) and 8(b) emerge the coincident peaks with the CO_2 peaks. Although the areas under CO_2 peaks are also the same, it expresses significantly different amounts of N_2 exposed during TPO with different oxidizing gases. This result implies that the higher amount of nitrogen may be attributed to nitrogen in gas phase (from NO feed) that can interact with carbonaceous deposits and form nitrogen products. Hence, nitrogen products observed were from both nitrogen-containing intermediate deposits and NO in gas phase. This is in agreement with the results reported by Chen et al. [32]. They suggested from the isotopic labeling technique applied on Fe-ZSM-5 that one nitrogen atom in every nitrogen produced came from the deposits; the other came from gas phase NO_2.

4. Conclusions

Investigation of the effects of NO and O_2 on the carbonaceous deposits over Cu-ZSM-5 reveals that a mixture of NO and O_2 accelerates both hydrocarbon deposition and removal. The presence of N_2 peaks coincident with CO_2 peaks during TPO suggests that the route of CO_2 formation may be due to the NO reduction mechanism, not the coke combustion. The aromatic domains exhibited in the IR bands together with the absence of graphitic phases by XRD observation confirm the formation of aromatic hydrocarbon deposits, not the graphite-like form.

Acknowledgements

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