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METHANOL CONVERSION TO HYDROCARBONS OVER H-ZSM-5: FURTHER EVIDENCE FOR THE ROLE OF NO

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Inhibition of the methanol to gasoline reaction induced by co-feeding of nitric oxide is compared and contrasted with inhibition by ammonia. It is concluded that NO does not act as a catalyst poison by being converted to NH_3. A mechanism for inhibition of the reaction by NO based on the Barton reaction is proposed.

1. Introduction

Since the original discovery that methanol could be converted into high octane gasoline over the zeolite catalyst H-ZSM-5 [1], considerable research attention has been focused on the elucidation of the mechanism of formation of the initial carbon-carbon bond. One recent proposal that has received some experimental support has been based on the involvement of free radicals [2] formed from the interaction of dimethyl ether with radical centres present in the zeolite structure. In previous studies [3–6] we have examined this proposal in some detail and, on the basis of the relative perturbation of dioxygen and nitric oxide on hydrocarbon formation, we have concluded that radical intermediates do not play a significant role in this reaction. The most significant observation was that nitric oxide, a stable π radical, did not inhibit or perturb the product distribution when co-fed with dimethyl ether, and no effect was observed in the timescale of our experiments [5,6] (ca 3 h, ZSM-5 $SiO_2/Al_2O_3 = 35$, 1% NO). In contrast, inhibition of hydrocarbon formation was observed when nitric oxide was co-fed with dimethyl ether over $WO_3/\gamma Al_2O_3$ [6] and we concluded that this catalyst could operate via a radical pathway. More recently, Chang [7] has made a detailed study of the effect of nitric oxide when co-fed with dimethyl ether over H-ZSM-5. Chang observed that nitric oxide could inhibit hydrocarbon formation following an induction period. The induction period was proportional to the SiO_2/Al_2O_3 ratio and the concentration of nitric oxide utilised, and the time utilised in our previous study had been too short to observe this effect [5,6]. On the basis of this new evidence, Chang concurred with the earlier proposals of Clarke et al. [2] that radicals were important in the initial carbon-carbon bond formation step. Chang noted that the involvement of nitric oxide was somewhat more complex as it acted as a source of catalyst poisons in addition to acting as a potential radical scavenger. In this respect, Chang considered that NH_3, formed by decomposition of the product of a Beckmann rearrangement [8,9], and methylamines, formed from methylation of NH_3 [10], could be the active poisons. In this paper we present our initial results of a further investigation into the effect of nitric oxide in the methanol conversion reaction, and in particular, we examine the relative effects of reaction inhibition caused by nitric oxide and ammonia.

2. Experimental

Zeolite H-ZSM-5 was prepared with a SiO_2/Al_2O_3 mole ratio of 90 according to the method of Howden [11]. Catalytic reactions were carried out in a laboratory microreactor as previously described [12]. Methanol and dimethyl ether were fed to the reactor in a carrier stream of nitrogen. When No and NH_3 co-feeding experiments were carried out the nitrogen carrier gas was switched to a nitrogen gas stream containing either NO or NH_3 at the required concentration. In this way the ratio of methanol, or dimethyl ether, to diluent was maintained and no corrections due to additional dilution was required. Satisfactory mass balance was obtained for all data presented and blank thermal reactions in the absence of catalyst were negligible under all conditions examined.

3. Results and discussion

Dimethyl ether was reacted over H-ZSM-5 ($SiO_2/Al_2O = 90$) at 400 °C and GHSV $= 2100\ h^{-1}$, a condition at which total reagent conversion is observed initially, in the presence and absence of co-fed NO (0.5 and 1.0 mole %) and the results are shown in table 1. In the absence of NO complete dimethyl ether conversion is maintained over H-ZSM-5 for over 300 mins. On addition of NO (0.5 mole %) to the dimethyl ether deactivation is observed after an induction period of ca 35 mins; at the higher level of 1.0 mole % NO the induction period was 25 mins. Similar results were observed for the reaction of methanol over this sample of H-ZSM-5. Our previous results [5,6] with NO co-feeding for a H-ZSM-5 with a higher aluminium content ($SiO_2/Al_2O_3 = 35$) indicated that no deactivation was observed up to ca 180 mins with 1–3 mole % co-fed NO. These results are therefore in broad agreement with the findings of Chang et al. [7]. It is important to note that the deactivation observed with NO under these conditions was irreversible and on removal of co-fed NO, following the occurrence of near complete deactivation, the conversion of dimethyl ether remained very low (table 1). Even if dimethyl ether is continued to be fed to the catalyst for 10 h following removal of NO, no increase in conversion is observed. In addition, NO pretreatment of the zeolite in the absence of dimethyl ether had no effect on the induction period for deactivation and, within experimental error, dimethyl ether conversion proceeded identically for both an NO pretreated H-ZSM-5 and an unpretreated catalyst. These data are therefore clear indications that NO interacts with a reaction intermediate formed from dimethyl ether, or methanol, to deactivate the catalytic sites.

In their previous study, Chang et al. [7] considered that NH_3, and consequently methylamines that are the product of a methylation reaction between NH_3 and surface methoxyl groups [13], could be a viable catalyst poison. To investigate this we have conducted a series of experiments in which NH_3 is co-fed at similar conditions to those employed for NO co-feeding, and the results are shown in table 2. At low levels of NH_3 co-feeding at 400 °C, no marked deactivation was observed up to 205 mins, whereas 0.5% co-fed NO deactivated the catalyst after an induction period of ca 25 mins (table 1). It was found that at this temperature much higher levels of NH_3 (5–10%) are required to induce any catalyst deactivation. The observed effect of NH_3, whilst acting as a catalyst poison, clearly contrasts with the effects observed for co-feeding NO, in that on a mole basis, NO is a more effective source of the catalyst poison than is NH_3. Hence, on this basis we conclude that NO does not interact with a reaction intermediate to form NH_3 as a catalyst poison via a Beckmann rearrangement pathway. In addition, the lack of any effect caused by pretreating the zeolite with NO indicates that the radical centres, known to be present [2], are not particularly important for this reaction. Further evidence that NO is not acting as a radical scavenger in this reaction can be obtained by contrasting its effects here with that obtained in NO co-feeding studies on the methane oxidation reaction [14]. This reaction is considered to occur via radical reactions initiated by radical sites on the oxide surface. Recent studies [15,16] in our laboratory have demonstrated that addition of low levels of NO during methane oxidation immediately decreases the methane conversion with no induction period. Removal of NO leads to an immediate restoration of the methane conversion, and this effect can be repeated a number of times without deleteriously affecting the catalyst. This type of behaviour would be considered normal for inhibition or perturbation of radical reactions on introduction of a radical species. In the methanol or dimethyl ether conversion

Table 1
Effect of NO addition on the conversion of dimethyl ether over H-ZSM-5 ($SiO_2/Al_2O_3 = 90$), 400 ° C, GHSV = 2100 h^{-1}

Reagent	Time on line (min)	Conversion to hydrocarbons (mole %)	Product selectivity (% by mass)							
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	C_{6+}
CH_3OCH_3	10	100	1.5	7.7	0.8	12.6	27.1	29.5	12.7	8.1
	120	100	1.7	10.1	0.6	17.1	19.5	29.8	13.7	7.5
	220	100	1.7	10.9	0.5	17.9	15.2	27.7	13.9	12.2
	270	99.8	1.7	11.2	0.5	18.3	13.6	26.2	13.7	14.8
CH_3OCH_3 [a] +0.5% NO	5	100	1.0	7.9	0.5	10.8	25.3	34.0	14.8	5.8
	7 (2)	100	1.1	8.9	0.6	12.8	26.3	32.4	12.9	5.0
	25 (20)	100	1.0	11.8	0.4	20.5	16.5	30.1	13.4	6.3
	40 (35)	99.9	1.2	15.9	0.3	24.3	13.8	29.7	8.2	6.6
	60 (55)	87.5	1.1	17.3	0.2	25.1	9.5	24.3	13.5	9.0
	110 (105)	1.9	3.3	2.1	0.3	3.2	0.5	2.3	8.7	79.6
	160 (115)	1.5	2.3	0.19	0.2	1.5	0.6	1.9	0.4	92.4
	200 [5]	1.2	4.7	0.8	0.3	1.3	0.7	1.9	0.1	90.2
	240 [45]	1.0	10.6	1.3	0.4	1.9	0.9	2.4	0.3	82.2
	285 [90]	1.1	9.1	1.2	0.4	1.7	0.9	2.0	0.3	84.4
CH_3OCH_3 [b] +0.5% NO	5	100	1.6	7.9	0.7	13.2	28.1	30.7	11.5	6.3
	45	100	1.6	8.6	0.7	15.0	22.9	30.5	14.0	6.7
	52 (2)	100	1.8	10.1	0.7	17.1	22.0	30.9	12.0	5.4

	70 (20)	100	1.5	12.7	0.5	23.1	15.1	28.6	13.0	5.5
	85 (35)	99.9	1.4	16.4	0.3	26.5	11.1	26.3	12.8	5.2
	100 (50)	87.5	1.3	20.1	0.2	30.9	5.9	21.8	12.8	7.0
	115 (65)	4.5	2.3	12.7	0.1	21.2	0.9	17.7	19.1	26.0
	145 (95)	2.0	2.8	1.2	0.2	1.9	0.6	4.2	21.6	67.5
	190 (140)	1.4	3.0	0.9	0.3	1.3	0.7	2.0	5.2	86.6
	240 (190)	1.1	3.1	0.8	0.3	1.2	0.8	3.2	1.3	89.3
CH_3OCH_3 [c] +1.0% NO	10	100	1.0	9.6	0.6	26.4	21.5	28.6	12.4	9.9
	55	100	1.1	10.9	0.5	20.1	17.2	29.2	11.8	9.2
	60 (5)	100	1.2	11.7	0.4	21.8	15.3	28.1	12.8	8.7
	70 (15)	100	1.1	12.9	0.3	23.8	11.7	27.2	12.9	10.1
	80 (25)	99.9	1.1	15.3	0.2	27.8	6.9	23.8	12.3	12.6
	95 (40)	64.7	1.0	15.3	0.1	30.7	5.0	20.8	12.0	15.1
	105 (50)	32.9	1.2	17.6	0.1	36.1	1.6	17.1	11.7	14.6
	115 (60)	2.1	1.9	5.0	0.3	9.6	1.5	13.7	16.3	51.7
	155 (100)	1.9	1.7	0.7	0.2	1.0	0.5	1.3	1.7	92.9
	200 (145)	1.4	1.6	0.6	0.2	0.8	0.6	1.9	0.4	93.9
	245 [40]	1.4	4.7	0.9	0.3	1.1	0.7	1.7	0.3	90.3
	285 [80]	1.2	6.6	1.2	0.3	1.4	0.8	2.1	0.2	89.4

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[a] NO (0.5 mole %) co-fed after 5 min and stopped at 195 min. Figures in parenthesis indicate time after NO co-feeding ( ) commenced and [ ] stopped.

[b] NO (0.5 mole %) co-fed after 50 min.

[c] NO (1.0 mole %) co-fed after 55 min and stepped at 205 min.

Table 2
Effect of NH_3 addition on the conversion of dimethyl ether over H-ZSM-5 ($SiO_2/Al_2O_3 = 90$), 400 ° C, GHSV = 2000 h^{-1}

Reagent	Time on line (min)	Conversion to hydrocarbons (mole %)	Product selectivity (% by mass)								
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	C_6	C_{7+}
CH_3OCH_3 + 0.5% NH_3 [a]	15	99.9	1.9	8.2	0.7	9.9	29.5	30.3	11.6	3.0	4.9
	85	100	2.7	10.1	0.7	12.7	25.2	30.6	11.7	2.8	3.5
	125	100	2.8	10.4	0.8	13.0	24.3	31.1	11.8	2.6	3.2
	165	100	2.9	11.9	0.7	14.2	22.4	29.4	12.0	3.0	3.5
	205	99.8	2.8	13.1	0.6	15.0	20.3	28.9	11.9	3.2	4.2
CH_3OCH_3 + 5.0% NH_3 [a]	15	100	2.4	5.3	1.1	5.8	39.4	31.1	11.1	2.5	1.3
	55	100	2.9	6.9	1.3	7.4	38.5	25.3	13.2	3.2	1.3
	95	100	3.6	9.1	1.4	9.8	25.9	33.6	12.9	2.4	1.3
	135	100	2.6	10.4	0.8	11.6	25.2	27.2	15.7	4.8	1.7
	175	99.6	2.7	13.5	0.8	15.4	23.4	28.0	11.6	3.0	1.6
	215	91.1	2.5	20.3	0.5	20.3	15.7	23.7	8.6	6.6	1.8
	255	6.6	9.5	0.6	0.2	4.4	1.5	27.5	34.9	9.6	11.8
	295	4.1	14.5	0.1	0.3	0.2	0.2	9.5	43.3	15.7	16.2
	335	2.6	22.9	0.1	0.4	0.3	0.2	0.4	17.1	28.3	26.7
CH_3OCH_3 + 10% NH_3 [a]	15	100	2.9	8.0	1.2	10.2	21.4	27.9	18.1	6.4	3.9
	55	43.5	3.0	9.1	1.0	11.1	18.7	31.7	15.0	4.9	5.5
	85	6.7	11.3	7.7	0.3	10.7	10.0	31.9	6.5	5.9	15.7

[a] NH_3 added from start of experiment.

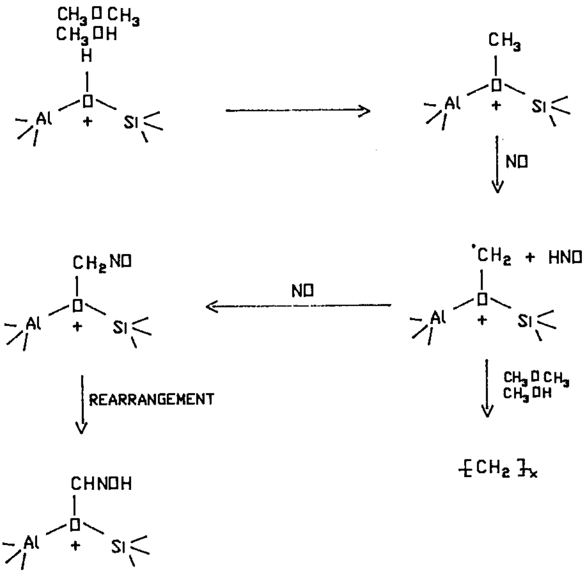

Fig. 1. Proposed reaction scheme for the effect of NO on dimethyl ether or methanol conversion.

reaction, deactivation is only observed after a considerable induction period and under these conditions is not reversible. On this basis we consider it unlikely that NO is acting as both a radical scavenger and a source of catalyst poisons in the methanol conversion reaction, as proposed by Chang et al. [7]. Based on the known chemistry of the interaction of NO with alkyl groups [17,18], we propose that interaction of NO with the methyloxonium intermediate, known to be present in the reaction from in-situ FTIR studies [13], would lead to the formation of a surface bonded nitroso compound (fig. 1), which would rearrange to an oxime [17,19]. The oxime could be expected to be both inactive and stable and would not readily desorb from the zeolite, and in this way formation of the oxime could lead to catalyst deactivation. Two interactions between NO and the surface intermediate are required to achieve deactivation (fig. 1), and hence this could account for the induction period, since the first abstraction of a hydrogen atom would lead to the formation of a radical ion intermediate that could still participate in hydrocarbon formation. In addition, the time required for deactivation would be directly proportional to both the NO and Al concentrations which is experimentally observed.

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