STUDY OF Fe/SILICALITE CATALYST FOR THE N_2O OXIDATION OF BENZENE TO PHENOL

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ABSTRACT

A set of Fe-silicalite samples of MFI structure have been prepared by the hydrothermal technique, followed by steaming and by further chemical treating of the solid. After characterisation by nitrogen sorption-desorption, XRD, SEM-EPMA, the samples have been tested as catalysts for the oxidation of benzene to phenol by N_2O. The best-performing catalyst has been studied also by TPD-TPR-MS, after preadsorption of both reactants and products. It was found that phenol forms when N_2O is adsorbed first, followed by benzene. Almost no phenol formation was observed when adsorbing benzene before N_2O. Furthermore, on this catalyst N_2O decomposed since 50°C or less, forming gaseous N_2 and adsorbed oxygen, which started to become available for the oxidation of benzene since 100-200°C. However, the so formed phenol remained adsorbed onto the catalyst. It desorbed within the 225-425°C temperature range, with a maximum around 300°C.

Keywords: Fe-silicalite catalyst, Benzene oxidation by N_2O, Preparation of phenol.

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INTRODUCTION

Panov and co-workers have studied extensively a particular class of iron-containing zeolites such as Fe/silicalites and FeZSM-5, which showed highly active for the benzene oxidation to phenol by N_2O [1-3]. From these investigations they suggest that the active sites should be a particular form of iron-complexes stabilised by the zeolite matrix [4]. Indeed, these active sites seem to be responsible of the low-temperature N_2O decomposition to a stable oxygen form, called α, adsorbed on the catalyst surface, which is reported to be the real oxidising agent [5,6].

Working on ZSM-5 zeolites, other researchers gave a different interpretation of the reaction mechanism, based on a correlation between catalyst acidity and activity [7,8]. The mechanism proposed involves either the protonation of N_2O by the zeolite or an activation of benzene by strong acid sites. Moreover, the steam-treating of the catalyst, described in these papers, is reported to create Lewis acidic extra-framework alumina, to which a higher catalytic activity should be connected. However, since a simple thermal treatment is sufficient to extract both aluminium and iron from the zeolite framework [9], this can be invoked for Panov's samples too, which contain both iron and aluminium.

In the present work we have prepared a set of Fe/silicalite catalysts, active for the oxidation of benzene to phenol by N_2O. The catalysts have been characterised by nitrogen adsorption/desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe micro analysis (EPMA) and catalytic activity testing. Furthermore, the best-performing catalyst was analysed by temperature programmed desorption-mass spectrometry (TPD-MS) and temperature programmed reaction-mass spectrometry (TPR-MS). The aim of the work was to investigate the N_2O decomposition on catalyst surface, to confirm the presence of adsorbed active oxygen species and to define the optimal temperature range for phenol formation.

EXPERIMENTAL

CATALYST PREPARATION

The catalysts were prepared by the hydrothermal method described in detail elsewhere[10]. Briefly, the Fe/silicalite catalyst A (Table 1) was prepared by mixing solutions of oxalic acid, ferric nitrate, sodium silicate and tetrapropylammonium bromide (TPABr). The gel so formed was let to crystallise into an autoclave at 170 °C for 4 days. The solid obtained was separated, washed, dried and calcined at 550 °C [11]. Ion exchange with a 1M NH_4NO_3 solution, to remove any different extraframework cation coming from the reagents, and decomposition of the ammonium precursor into the final, snow-white protonic form of the solid was achieved by calcination in air at 550 °C.

Catalyst B was prepared by steam-treating catalyst A at 550 °C with a 75% (mol) steam in nitrogen stream. The final product was light-brown.

Catalyst C was prepared by treating catalyst B with a $Na_2S_2O_4$/NaCl solution and then with a HNO_3/NH_4NO_3 buffer solution, followed by calcination in flowing air at 550 °C. The main properties of the catalysts prepared are reported in Tab. 1.

CATALYST CHARACTERISATION

Specific surface area and porosity were determined by means of a Micromeritics ASAP 2010 instrument, by nitrogen adsorption-desorption. Structural analysis was carried out by X-ray Diffraction (XRD) by means of a Philips PW 1820 powder diffractometer and employing the Cu(Kα) radiation (λ=1.54056 Å). The comparison with literature data [12] confirmed the presence of the MFI structure only. Quantitative elemental analysis, morphology and size of the crystals were obtained by means of a Leica-Oxford Link-Isis (mod. LEO 435 VP) scanning electron microscope-electron probe micro analyser (SEM-EPMA). Catalytic activity and selectivity for the oxidation of benzene to phenol by N_2O were tested by means of a continuous stainless steel tubular reactor at 350°C and atmospheric pressure. The catalyst was pressed into wafers, ground and sieved into 0.15-0.25 mm particles and then loaded after dilution 1:2 (vol/vol) with quartz powder of the same particle size. Prior to each run the catalyst was activated in flowing helium at 550 °C for 4 h. A mixture of benzene (FLUKA, purity ≥ 99% vol.), N_2O (SAPIO, purity ≥ 99.99% vol.) and He (SAPIO, purity ≥ 99.9995% vol.) in 5:20:75 molar ratio, respectively, was fed. The gas flow rates were measured and regulated by means of MKS mod. 258C mass-flow regulators, while benzene was fed through a mod. 314 ISCO metering pump. Temperature was regulated by an EUROTHERM (model 812) TRC. Samples of the product for analysis were collected in glass traps, cooled down to –40 °C by means of a cryogenic system (Neslab mod. CC-65 II). The product obtained after 3 and 6 h on-stream was analysed by gas-chromatography (HP model 5710A FID apparatus). The results were expressed as benzene conversion and selectivity to phenol.

TPD analysis was carried out on the most active catalyst only (sample C), as mentioned. N_2O decomposition and desorption properties of reactants and products were investigated. The apparatus has been described in detail elsewhere [13]. Briefly, the catalyst powder was loaded in a continuous quartz microreactor. The temperature programme was controlled by means of an EUROTHERM (model 822) TRC. The outlet gas was analysed by means of a quadrupolar mass-spectrometer (PPT Residual Gas Analyzer, by MKS Instruments). The mass fragments chosen were m/z=30 for N_2O, in order to avoid confusion with CO_2 (m/z=44), m/z=78 and m/z=94 for benzene and phenol, respectively. The final temperature selected for every TPD experiment was 500°C, with a ramp of 10 °C/min, while the starting and the pre-adsorption temperature was 50 °C for N_2O, 350 °C for benzene and 300 °C for phenol.

N_2O saturation was achieved by feeding (20 cm^3/min for 6 h) a gas mixture of 1% N_2O in helium, while adsorption of both benzene and phenol (re-distilled from the ≥99 wt.% pure reagent) was performed by injecting successive 0.5 μl pulses till saturation. Before any TPD experiment an activation pre-treatment in flowing He at 500 °C was carried out, while at the end of every TPD run the catalyst was regenerated in flowing air, in order to burn out any trace of tar and coke.

A further investigation on N_2O decomposition was carried out by TPR, under the same saturation conditions reported for TPD, but employing 1% N_2O in He both as carrier and reactant gas.

On catalyst C a further analysis was carried out aiming at determining the temperature range for phenol formation. The same apparatus used for the TPR analysis was employed, by substituting N_2O (20 cm^3/min) for He as carrier gas. The same pre-treatment in flowing He at 500 °C was adopted before the run, in order to activate the catalyst. The reaction was performed by injecting pulses (1.5 μl) of benzene while running a temperature programme from 200 °C to 500 °C, with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Choice of the catalyst preparation method

A careful analysis of literature [2,4-6] indicates that active and selective catalysts can be obtained when Fe forms some special clusters outside the zeolitic lattice, but inside the zeolitic pores. Such clusters seem to form preferentially by extraction of Fe from the framework. Indeed, a set of catalysts, prepared by us by ion exchange of commercial zeolite samples with Fe solution showed only negligibly active.

To force iron into the zeolitic lattice during preparation of Fe-silicalite, one has to avoid iron hydroxide precipitation during the formation of the precursor gel [9,10]. To this end oxalic acid can be added to the iron solution, obtaining a complex stable towards Fe hydroxide precipitation during the addition of the solution of silica precursor and of template. An alternative way [10] is dropping the silica precursor into an acidic solution of iron salt. This procedure was followed for the preparation of other samples and no appreciable difference in catalytic performance was noticed. The silica source was a low molecular weight sodium silicate solution, which is reported [9,10] to favour iron incorporation. The snow-white colour of the solid obtained indicates that no appreciable extraction of framework iron had occurred.

Steam treatment is reported as able to extract iron from the zeolite matrix in a controlled way [9]. The extent of this phenomenon is correlated to the duration of steaming and to the steam concentration in the gas flow [3]. Extraction of Fe can be achieved also by thermal treatment in inert atmosphere or by leaching by a suitable complexing agent such as $Na_2S_2O_4$, though less effectively. The immediate evidence of the extraction is the progressive change of the colour of solid, from white to brownish, to increasingly deep brown. The extraction extent has been monitored by IR analysis, as reported in a parallel work [14].

Characterisation of catalysts

The EPMA analysis and N_2 adsorption/desorption data (Tab.1) showed that no appreciable difference in Fe content of the three catalysts was observed and that both surface area and porosity progressively increased on passing from catalyst A to B to C, the micropore volume fraction (with respect to the total pore volume) remaining constant. In this analysis the t-plot correlation through the Harkins-Jura equation was considered more reliable than the BET equation for microporosity estimation. Hence, it may be argued that the iron extracted out of the zeolitic matrix by steam treatment is not leached out of the zeolitic crystals. It simply tends to form Fe oxide microparticles within the zeolite pores, as shown by the change in colour from white to brownish. This extraction is accompanied by an increase of both porosity and surface area (compare samples A and B, Tab.1). However, during steaming, the extraxted Fe oxide tends to form relatively bulky extraframework clusters. $Na_2S_2O_4$ is well-known as an effective complexing agent of Fe. Hence, the successive treatment with $Na_2S_2O_4$/NaCl solution does not leach Fe out of the solid. Very likely it extracts a further amount of Fe from the matrix and dissolves the previously formed Fe oxide clusters, redistributing Fe in much smaller clusters within the zeolitic pore network, with a further increase of both surface area and porosity. The results of the activity tests confirm this hypothesis, the catalytic behaviour being determined apparently by the nature and position of the active sites, rather than by Fe amount.

The effect of the preparation method and of both steaming and chemical treatment on crystalline structure, morphology and crystal size, has been evaluated by XRD (Fig.1) and SEM analysis. All the samples showed the XRD pattern typical of MFI [12] and no structure change seems to have occurred after any of the mentioned treatments. A further confirmation comes from SEM analysis. The same crystal shape and size (about 800-1000 nm) was maintained for all the catalysts. We can conclude that both steaming and chemical treatment didn’t affect significantly the structural characteristics of our samples.

However, the presence of any tetrahedrally coordinated trivalent ion in the zeolitic framework generates an acidic site, which deeply affects the catalytic behaviour of the solid. Indeed, it is well-known [1-3] that the main drawback of catalysts for the present process is the simultaneous presence of cracking-coking reactions, triggered by the acid sites of the catalyst. So, the more deeply Fe ions are extracted from the framework, the less acidic is the catalyst. Once extracted from the matrix, Fe ions do not generate acidity any more. Therefore, the generation of the active Fe-based small extraframework clusters, by steaming and further chemical treatment is accompanied by a correponding decrease of acidity, which reflects on an increase of both stability and selectivity to the desired product. A detailed analysis of the change in acidity following such treatments and corfirming this behaviour of our samples, has been carried out in a parallel work by IR analysis and reported elsewhere, as mentioned [14].

Optimisation of reaction parameters

Preliminary test-runs were carried out in order to define the optimal reaction conditions and a standard method for catalyst testing. Different benzene/N_2O molar feeding ratios were checked: 5/1, 1/2 and 1/4. The last value gave the best results. Indeed, by increasing this feeding ratio a selectivity decrease and a more rapid deactivation by coke formation was observed.

The hydroxylation reaction is highly exothermic ($\Delta H°_r$ = -261 kJ/mol) [15]. So, the formation of a hot-spot of 30-40 °C was observed. An uncontrolled temperature rising causes a decrease in phenol selectivity and a more rapid coking of the catalyst. Hence, besides catalyst dilution with quartz, a high thermal conductivity gas such as helium was selected as diluent.

The reaction temperatures usually reported in literature [16] range between 300 and 400°C, though on pilot scale higher values have been reported [1]. After various tests, not reported for brevity, a standard temperature of 350 °C was chosen for the present tests. Contact time (vol. of catalyst bed per vol. of fed gas per second) values usually reported in patent literature range between 0.25 and 4 s. In our experience, lower values of this parameters gave better results in terms of both selectivity and catalyst resistance to deactivation. So, a standard time factor of 0.5 s was adopted.

As reported in most of the previously cited literature, the catalyst was completely and repetitively regenerable. In our experience a 3 h treatment in flowing air at 550°C was sufficient to restore the original catalytic activity.

Activity tests

A support for all the previously mentioned hypotheses comes from the comparison of the performance of catalyst B and C (Tab. 2). After 3 h on-stream catalyst C showed only slightly more active than catalyst B and comparably selective. However, after 6 h on-stream catalyst C showed much better than catalyst B. The latter, indeed, maintained rather the same conversion (11%) with respect to 3 h on-stream (10%), but selectivity dropped from 97 to 54%. By contrast, catalyst C maintained a high selectivity (from 98 to 100%), though benzene conversion dropped from 12 to 5%. These results seem to confirm that iron extraction from the framework can be indicated not only as the primary cause of formation of the active sites, responsible of a high selectivity to phenol, but also of the considerable change of surface acidity of the catalyst, responsible of the undesired cracking-coking side reactions. Hence, the different behaviour of catalyst B and C is perfectly in line with these findings.

TPD-TPR-MS analysis

This analysis was performed on the best-performing catalyst only (sample C) in order to investigate its adsorptive properties with respect to the species involved in the reaction. According to Panov [5,6,17], on Fe-based active sites a low-temperature catalytic decomposition of N_2O would occur and a particular form of oxygen, referred to as α, would form. The latter starts to desorb at 100-150°C, becoming available for the oxidation of benzene. The TPD-MS technique proved a helpful device to investigate these phenomena. In Fig.2*a* the typical TPD-MS pattern is reported, relative to the oxygen signal (m/z=32), after pre-adsorption of N_2O at 50°C and employing He as carrier gas. An intense desorption at 100-200°C may be observed. This confirms the N_2O decomposition, occurring during the pre-adsorption phase at 50°C. No difference was noticed when employing pure N_2O rather than a mixture of 1% N_2O in He during the low-temperature pre-adsorption step. The adsorbed oxygen in the present work desorbs at considerably lower temperature, with respect to that (300°C) reported by Panov and co-workers [17]. A further TPR experiment, carried out under the same pre-adsorption conditions, but using

1% N_2O in He gas mixture both as reagent and carrier gas, showed an oxygen desorption peak analogous to the previously mentioned one (Fig.2*b*). The oxygen evolution, taking place at higher temperature (about 430°C) was interpreted as due to catalytic decomposition of gaseous N_2O, not involved into the benzene oxidation reaction. Indeed, the latter takes place at a much lower temperature, with respect to the thermal decomposition of N_2O, which in the absence of catalyst occurs at about 600°C only.

Separated adsorption of benzene and phenol was carried out by injecting 0.5 μl pulses at 350 or 300°C, respectively. The choice of these pre-adsorption conditions was based on a compromise between the too slow release of both adsorbates at low temperature and their tendency to decompose at high temperature, leading to coking and fouling of the catalyst surface. From the benzene (m/z=78) TPD-MS analysis, a wide desorption peak was observed between 380 and 550°C, accompanied by a weak H_2 (m/z=2) formation, probably due to a partial dehydrogenation-cracking of the reactant. The desorption of pre-adsorbed phenol (m/z=94) was observed between 300 and 500°C, with a maximum around 400°C. Also in this case a broad and very weak signal relative to H_2 (m/z=2) was detected.

The optimal temperature range for phenol recovery in the gas outcoming from the reactor was determined through pulsed TPR analysis. Though forming very likely at much lower temperature (100-200°C), phenol remains adsorbed onto the catalyst surface at least up to 220°C, so inhibiting the further adsorption of reactants. Indeed, as shown in Fig.3, the appearance of phenol (m/z=94) in the TPR spectrum started at ca. 225°C, ending at ca. 425°C, with a maximum around 300°C. Therefore, phenol desorption and recovering took place at temperatures higher than those of oxygen complete desorption (*vide supra*). This analysis was done without N_2O pre-adsorption, at temperatures higher than those found both for N_2O catalytic decomposition and for oxygen desorption. Hence, at the temperatures adopted in our TPR-MS analysis oxygen was immediately available for the reaction.

Furthermore, the slow benzene release below 250°C affected reaction selectivity, because a high contact time favours the secondary decomposition reactions. This was confirmed also by broad peaks relative to the m/z=39 signal, corresponding to a typical fragment of the benzene ring. This fragment was always present and more intense than the molecular peak. A similar behaviour was observed with phenol too, confirming the decomposition of both benzene and phenol within the explored temperature range. The hydrogen signal corresponding to every benzene or phenol pulse is due to the same undesired secondary reactions.

CONCLUSIONS

In the present work an active and selective Fe/silicalite catalyst for benzene oxidation to phenol by N_2O was prepared. Post-synthesis thermal and chemical treatments of the catalyst were then studied and their effect on catalyst performance was investigated. Through TPD-MS analysis the decomposition of N_2O at very low temperatures and the presence of a particular oxygen species adsorbed on catalyst surface were confirmed. This oxygen starts to desorb at 100-200°C. Finally, the optimal temperature range for phenol formation and recovery in the reactor outlet gas has been identified.

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Table 1: Main physico-chemical properties of the catalysts prepared. Crystal diameter 0.5-1.0 μm.

Catalyst	Fe (wt. %)	SA (m^2/g)	Total pore Vol.* (cm^3/g)	Micropore Vol.** (cm^3/g)
A	1.03	353	0.163	0.150
B	0.99	418	0.206	0.187
C	1.06	462	0.228	0.208

* Values measured at $P/P_o=0.986$

** Values obtained using the t-plot method with the Harkins-Jura equation.

Table 2: Conversion of benzene and selectivity to phenol of the catalysts employed for benzene oxidation by N_2O. Testing conditions: 350 °C, atmospheric pressure, $C_6H_6 : N_2O : He = 5 : 20 : 75$ molar ratios. Analysis after 3 and 6 h on-stream. Contact time=0.5 s.

Catalyst	3 h on-stream		6 h on-stream	
	Conversion %	Selectivity %	Conversion %	Selectivity %
A	16	36	18	24
B	10	97	11*	54*
C	12	98	5	100

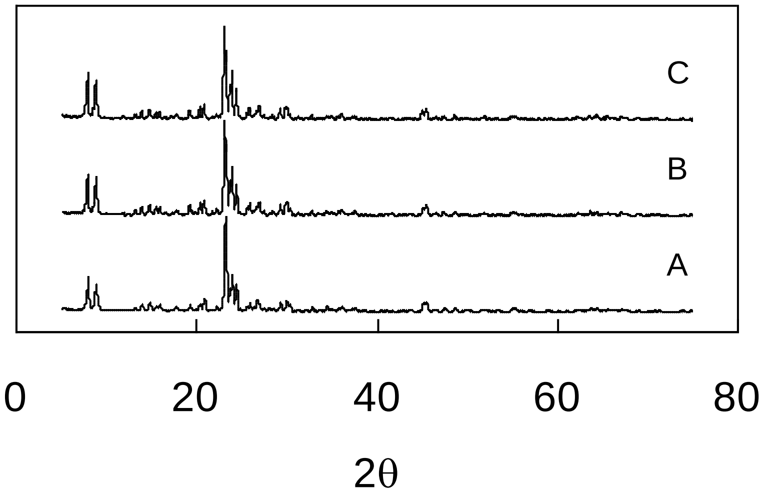
* Time-on stream = 5 h.

FIGURE CAPTIONS

Fig. 1: XRD patterns relative to catalyst A, B and C (Table 1).

Fig. 2: O_2 signal (m/z=32) of TPD-MS analysis on catalyst C after pre-saturation with N_2O by flowing a 1% N_2O in He gas mixture. Carrier gas: (a) Pure He, (b) 1% N_2O in He.

Fig. 3: TPR-MS analysis on catalyst C. Pure N_2O as carrier and reactant gas. Appearance of phenol (m/z=94) in the carrier gas after each 1.5 μl pulse of benzene.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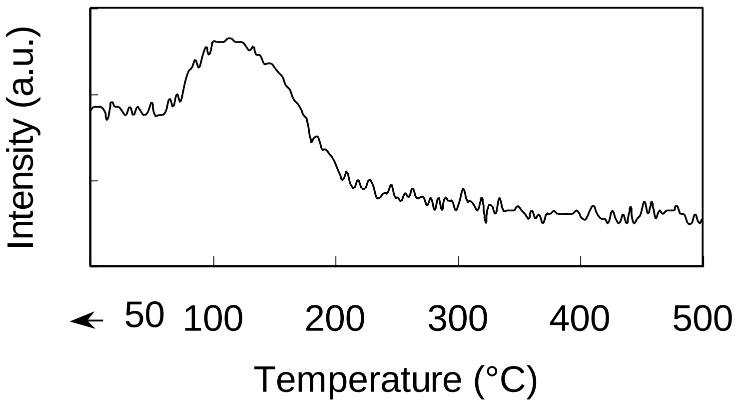
a)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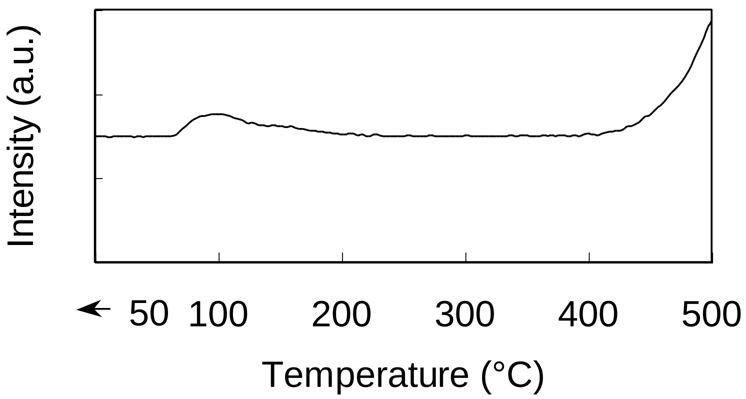
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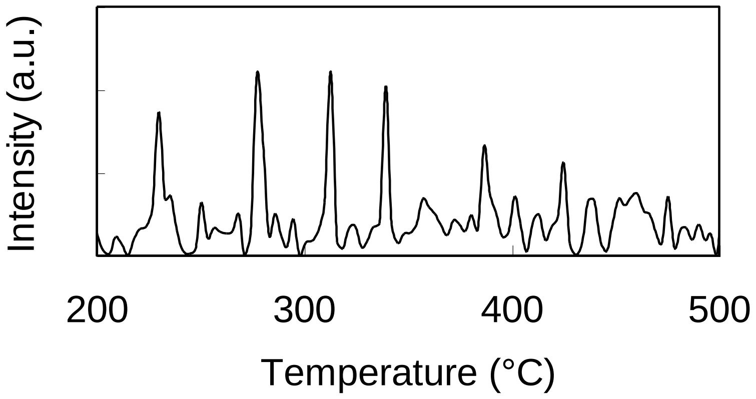
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