



INFLUENCE OF SULPHUR DIOXIDE AND HALOGENATED ACIDS UPON BENZENE CONVERSION ON SCR-DeNO_x COMMERCIAL CATALYST♦

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Abstract: In the presence of SCR-DeNO_x commercial catalyst with low content in active component (0.53 % wt. V₂O₅), specific to treatment of gas emissions containing nitrogen oxides, benzene oxidation is possible. Benzene catalytic conversion can be influenced by the presence of the other components of the gas emission. In this paper, the experimental results concerning the influence of halogenated acids (HCl, HBr) and sulphur dioxide on benzene behaviour during oxidation in humid air stream (5 % vol. H₂O) and defining of the reaction products are presented. Experimental study was conducted on a laboratory set-up operated in continuous regime, at temperatures of 573 – 623 K and for a gas spatial velocity equal to 6400 h⁻¹. Oxidation of benzene, present in low concentration in the gas (80 – 100 ppm C₆H₆) is partial, the catalytic selectivity towards carbon dioxide forming being approximately 60 %. The presence of halogenated acids and sulphur dioxide determines a supplementary consumption of benzene, as a result of substitution reaction with participation of benzene ring that leads to formation of some aromatic derivatives.

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INTRODUCTION

In the study regarding the catalytic destruction of aromatic volatile organic compounds existent in emissions resulted from municipal and medical waste thermal incineration, benzene was used as model molecule. The complex composition of these emissions (NO_x, SO₂, HCl, HF, CO, heavy metals and mineral pollutants [1]) may influence benzene catalytic conversion toward secondary pollutants formation. The aromatic volatile organic compounds may result partially by incomplete combustion of the fuel used for incineration and partially through plastics burning [2 - 3]. The formed aromatic hydrocarbons may be monocyclic or polycyclic, among them, the halogenated derivatives, biphenyls, dioxins and furans are considered as being very toxic for human health.

For this reason, the European legislation regarding the sources that emit aromatic organic pollutants is more and more severely and foresees a maximum admissible concentration for total organic carbon equal to 10 mg C/Nm³, and a limit value of 0.1 ng I-TEQ/Nm³ (International Toxicity Equivalents) for dioxins and furans, respectively [4]. The depollution of the gases resulted from waste incineration involves the selective catalytic reduction (SCR) of nitrogen oxides in the presence of ammonia injected in the treated gas flow [1, 5]. The catalysts are mostly based on V₂O₅-WO₃/TiO₂ (anatase).

The active sites (centres) are considered to belong to the vanadium oxide phase although tungsten oxides act as activation and structure-stabilizing agents. Moreover, WO₃ insertion increases the Brønsted acidic character of the surface, allowing an increased catalyst resistance to sulphur dioxide attack [6]. In typical high-dust configuration power plants, the V₂O₅ content is generally low (< 1 %wt. V₂O₅ [7]) in order to limit the concomitant oxidation of sulphur dioxide to sulphur trioxide. Finally, this leads to the formation of ammonium sulphates, which can condense on the catalyst itself or on cold plant parts after the reactions. Due to the low V₂O₅ amount, the reaction temperature is in the range 473 – 673 K [6 - 8].

In the presence of V₂O₅-WO₃/TiO₂ catalyst, which is typical for the SCR-DeNO_x process, also the oxidation of aromatic volatile organic compounds and halogenated derivatives is possible [9 - 13].

The aim of this work is to analyze the benzene behaviour in oxidation on SCR-DeNO_x (V₂O₅-WO₃/TiO₂, with 0.53 %wt. V₂O₅) commercial catalyst in the presence of other pollutants that are specific to emissions resulted from waste incineration. The laboratory study, carried-out at temperatures ranged between 573 and 623 K, aimed at establishing the influence of halogenated acids and sulphur dioxide presence on benzene catalytic conversion in oxidation reaction in humid air stream, and defining of the reaction products.

EXPERIMENTAL

The catalytic tests were conducted in the presence of V₂O₅-WO₃/TiO₂ commercial catalyst that is specific to SCR-DeNO_x processes in high-dust system. The high-dust

system can be applied when the dust and sulphur dioxide content in the waste gas are sufficiently reduced to allow the direct feed of the waste gas into the SCR-DeNOx reactor [1, 5].

The catalyst was used in its commercial form, prepared by co-precipitation (IHI – Japan), containing 0.53 % wt. V_2O_5 (active component) and 7.7 % WO_3 (promoter) on TiO_2 – anatase support. The commercial monolith exhibits straight channels by square section, with step of 4.95 mm and wall thickness of 1 – 1.3 mm and a specific geometric surface area is $555.5 \text{ m}^2/\text{m}^3$. A catalytic element consisting in 3×3 channels, having a length of 11 cm and a volume equal to 27.634 cm^3 , was used within the experiments.

Benzene catalytic oxidation reaction at concentrations of 80 – 100 ppm C_6H_6 into the gas was accomplished in humid air stream, containing 5 % vol. H_2O . The investigation of the influence of halogenated acids and sulphur dioxide was carried-out for the following concentrations: 260 ppm HCl or 260 ppm HBr and 350 ppm SO_2 .

Experimental data concerning gas concentration before and after the catalytic reaction were achieved on a laboratory set-up operated in continuous regime at temperature of 573 – 623 K and for a gas spatial velocity equal to 6400 h^{-1} . Working procedure for achievement of experimental data is presented in figure 1.

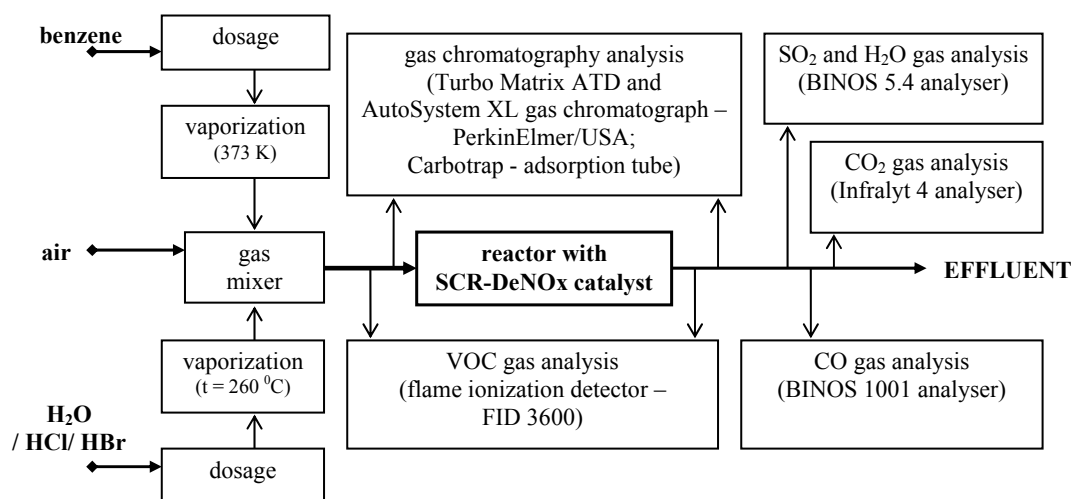


Figure 1. Working procedures for achievement of experimental data.

Catalytic reactor consists in two concentric quartz tubes (diameters of 40 x 1.5 mm, 32 x 1.5 mm, respectively), placed into an electrically heated oven. The incoming simulated gas flue gas was heated in the outer ring cylinder to the required reaction temperature before its flow was reversed and returned in the inner cylinder of the reactor, where is inserted the honey comb shaped SCR-DeNOx catalysts test element. Inside the monolith catalyst from the reactor, a thermo-element (Ni-Cr-Ni) was inserted, which was connected to a computer, the reaction temperature being, thus, monitored on-line.

Analysis of benzene concentration from initial and final samples was done by chromatographic analysis on Carbotrap 349 (Supelco/USA) type column using thermal desorber Turbo Matrix ATD connected in series with AutoSystem XL (PerkinElmer/USA) gas chromatograph. The specific reactive necessary for gas

chromatography calibration and conducting experiments were provided by Merck/Germany (benzene with 99.7 %, chlorobenzene with 99 %, 1,2-dichlorobenzene with 97 %, 1,3-dichlorobenzene with 97 %, 1,4-dichlorobenzene with 99%, bromobenzene with 99 %, 1,3-dibromobenzene with 97 %,) and Aldrich/Germany (1,2 dibromobenzene with 98 %, 1,4-dibromobenzene with 98 %). The hydrobromic acid (47 %) and hydrochloric acid (37 %) were both obtained from Merck.

The flame ionization detector FID Modell 3600 from Bernath Atomic/Germany was used to determine the concentration of organic compounds in propane-carbon equivalents in the influent and effluent gases in the flow reactor. The other components from the gas (CO, CO₂, SO₂) were analysed by the help of gas analysers (Binos 1001, Binos 5.4, Infralyt 4/Germany). For calibration purposes reference gases with 405 ppm SO₂ in synthetic air obtained from Messer/Germany, 774 ppm CO₂ and 400 ppm CO respectively, in nitrogen from Linde/Germany were used during the investigation.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Interpretation of the experimental results was achieved considering the following aspects: a) establishment of halogenated acids (HCl, HBr) influence on benzene catalytic oxidation in humid air stream and defining of the reaction products; b) establishment of sulphur dioxide influence on benzene behaviour in catalytic oxidation, both in the presence in and absence of halogenated acids.

Conversion is defined by the ratio between the amount of transformed reactant and initial amount of reactant subjected to catalytic transformation.

Influence of gas composition upon benzene conversion on SCR-DeNO_x (0.53 % wt. V₂O₅) commercial catalyst is presented in figure 3. Benzene catalytic oxidation reaction in humid air stream (5 % vol. H₂O) occurs with conversion above 55 % at temperature of 573 K, reaching up to 75 % at temperature of 623 K. Halogenated acids (260 ppm HCl or 260 ppm HBr) have a positive influence on benzene conversion, leading to the increase of benzene consumption that is more accentuated in the case of hydrobromic acid (figure 2.a).

Presence of sulphur dioxide (350 ppm SO₂) in the gas subjected to catalytic treatment determines an increase of benzene conversion, this exceeding the values of 80 % at temperature of 573 K and 90 %, respectively, at 623 K (figure 2.b). Influence of SO₂ on benzene conversion is almost similar, no matter of the composition of the gas system.

From analysis of gas composition after catalytic reaction, one can observe that benzene oxidation reaction is partial, reaction products containing above 75 % carbon dioxide and monoxide. Water vapours existent in the catalytic treated gas determine a catalytic selectivity towards oxidation reaction with CO₂ formation, approximately 60 %.

In table 1, the mass balance for benzene oxidation reaction at temperature of 573 K, in function of gas composition, is presented.

Although the halogenated acids lead to increase of benzene conversion, these ones determine formation of other pollutant compounds, as mono- and di-halogenated derivatives. Consequently, in the presence of halogenated acids the selectivity of reaction with CO₂ formation decreases. This may be explained by the fact that benzene participates easier in halogenation reaction than in the oxidation one.

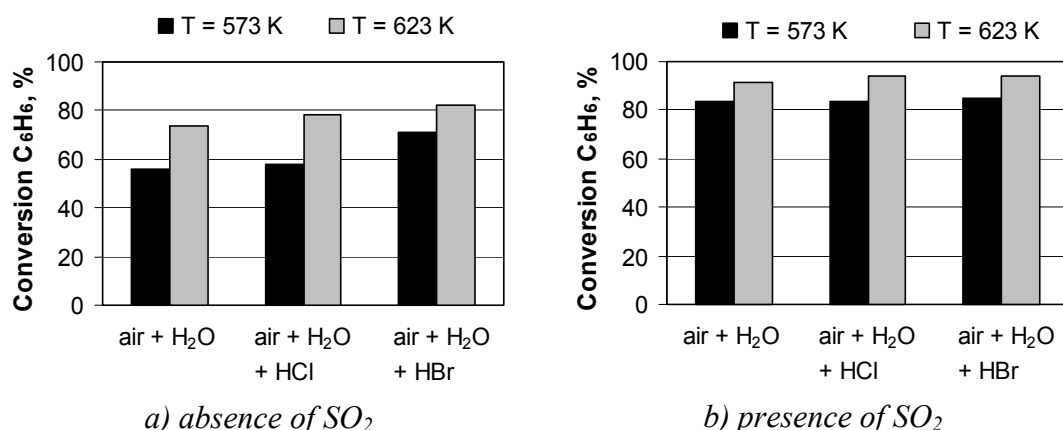
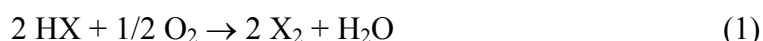


Figure 2. Influence of halogenated acids and sulphur dioxide on benzene conversion in oxidation reaction in humid air stream (5 % vol. H₂O) on SCR-DeNO_x (0.53 % wt. V₂O₅) commercial catalyst

Table 1. Mass balance for benzene oxidation reaction on SCR-DeNO_x (0.53 % wt. V₂O₅) commercial catalyst, at temperature of 573 K

Parameters	U.M.	Oxidation conditions		
		air + H ₂ O	air + H ₂ O + HCl	air + H ₂ O + HBr
$c_{C_6H_6}^0$	ppm	94.5	92.0	91.8
$x_{C_6H_6}$	%	56.3	57.3	68.5
$c_{CO_2}/c_{C_6H_6}^0$	mol/mol	1.52	1.44	1.57
$c_{CO}/c_{C_6H_6}^0$	mol/mol	1.06	1.12	1.18
$S_{CO_2/CO}$	%	59	56	57
$\eta_{C_6H_6}$	%	42.9	42.6	45.8
CO + CO ₂ in gas	%	76.3	74.4	66.9

Benzene halogenation is possible as a result of a halogens formation by halogenated acids oxidation reaction:



The calculus of thermodynamic equilibrium for halogenated acids oxidation reaction (achieved with the FACTSAGE version 5.3.1 programme – GTT Technology Germany) led to conclusion that the possibility of chlorine formation through hydrochloric acid is less comparative to that of a bromine formation.

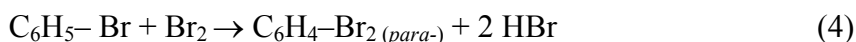
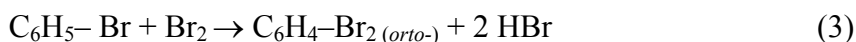
From the data presented in the table 2 may be observed that the possibility of chlorine forming from oxidation was slower compared to that of bromine formation. This behaviour may explain why benzene catalytic conversion in oxidation reaction in the presence of HBr is superior to that obtained in the case of HCl presence. Benzene conversion in the presence of HCl is sensible equal to that obtained in catalytic oxidation reaction in humid air stream.

In the presence of halogens, benzene easily participates in electrophilic substitution reaction, with formation of mono-halogenated and di-halogenated derivatives. The substituent from the benzene ring influences the reactivity of the latter towards the electrophilic reactant and determines the place where the attack takes place.

Table 2. Thermodynamic equilibrium for halogenated acids oxidation reaction
(air, 5 % vol. H_2O , 260 ppm HCl , 260 ppm HBr)

Temperature, K	Conversion, %	
	$2 HCl + 1/2 O_2 \rightarrow Cl_2 + H_2O$	$2 HBr + 1/2 O_2 \rightarrow Br_2 + H_2O$
523	37	100
573	19	100
623	9	99.9

Halogens belong to first order electrophilic substituent group, orienting the substitution in *ortho*- and *para*- positions of aromatic ring [14], concordant to reaction:



At low concentration of halogens, the reaction leads, mainly, to appearance of mono-halogenated derivative.

Investigation on the formation of brominated benzenes in a gas containing benzene and HBr with and without the addition of SO_2 where conducted, the results are presented in figure 3.

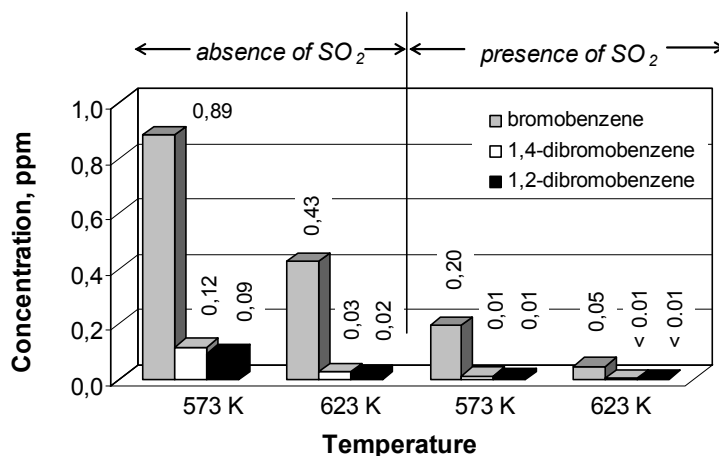
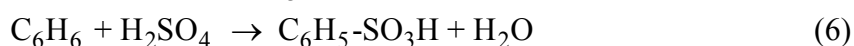
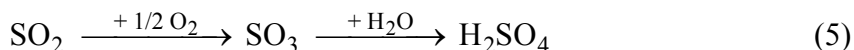


Figure 3. Influence of SO_2 on formation of halogenated derivatives in benzene catalytic oxidation reaction in the presence of halogenated acids
(air, 90 ppm C_6H_6 , 5 % vol. H_2O , 260 ppm HCl , 260 ppm HBr , 350 ppm SO_2)

From analysis of reaction products resulted in the case of benzene catalytic oxidation in humid air stream, in the presence of hydrobromic acid, at temperature of 573 K, a concentration lower than 1 ppm mono-bromobenzene and almost 0.2 ppm di-brominated derivatives (*ortho*- and *para*-) were obtained.

In the case of sulphur dioxide presence, benzene supplementary consumption is

attributed to substitution reaction of this one with the products resulted in SO₂ catalytic oxidation. It was experimentally observed that in the presence of SCR-DeNO_x (0.53 % wt. V₂O₅) catalyst, sulphur dioxide consumption exists that yields in conversions of 5 – 10 %. Sulphur dioxide may oxidize to sulphur trioxide, further forming sulphuric acid in the presence of water vapours. The latter may react with benzene through a substitution reaction forming benzenesulphonic acid [14]. Hence, apart of benzene oxidation reaction with formation of CO₂, CO and water vapours, benzene sulphonation reaction also occurs:



Thus may explain why in the presence of sulphur dioxide into the catalytic treated gas, benzene consumption is higher.

The presence of sulphur dioxide, alongside the halogenated acids, substantially reduces the content in halogenated derivatives resulted from reaction with benzene. This underlines the higher affinity of benzene for sulphonation reaction compared to the halogenation one.

CONCLUSIONS

For the studied temperature range (573 – 623 K), benzene catalytic oxidation on SCR-DeNO_x (V₂O₅-WO₃/TiO₂, with 0.53 % wt. V₂O₅) commercial catalyst is partial, with formation of above 75 % carbon dioxide and monoxide in reaction products. Catalytic selectivity towards carbon dioxide forming is approximately 60 %. This is slowly diminished by the presence of halogenated acids and sulphur dioxide.

Halogenated acids increase benzene conversion but bring into the system a new class of pollutants: mono- and di-halogenated derivatives. In this case, decrease of selectivity towards carbon dioxide forming is explained by the ease of benzene participation in halogenation reaction compared to oxidation one.

Presence of sulphur dioxide into the gases leads to increase of benzene conversion with 10 – 25 %, in comparison to the case of its absence. Benzene supplementary consumption is attributed to substitution in the presence of sulphuric acid, which may appear as a result of catalytic oxidation of sulphur dioxide to sulphur trioxide. Conversion of sulphur dioxide on the studied catalyst is of 5 – 10 %. Sulphur dioxide inside the gases exhibits a favourable influence not only upon benzene consumption, but also on the content of halogenated derivatives that may be formed in the presence of halogenated acids. Substantial reduction of the content of de halogenated derivatives underlines the higher affinity of benzene for sulphonation reaction compared to the halogenation one.

NOTATIONS

$x_{\text{C}_6\text{H}_6} = (c_{\text{C}_6\text{H}_6}^0 - c_{\text{C}_6\text{H}_6}) / c_{\text{C}_6\text{H}_6}^0$ – conversion of benzene; $S_{\text{CO}_2/\text{CO}} = c_{\text{CO}_2} / (c_{\text{CO}} + c_{\text{CO}_2})$ – catalytic selectivity in the oxidation reaction; $\eta_{\text{C}_6\text{H}_6} = (c_{\text{CO}} + c_{\text{CO}_2}) / (6 \cdot c_{\text{C}_6\text{H}_6}^0)$ – degree of

benzene transformation; $c_{C_6H_6}^0$ – inlet concentration of benzene, ppm; $c_{C_6H_6}$, c_{CO_2} , c_{CO} – concentration of gas component i (C_6H_6 , CO_2 , CO), ppm; $SV = V_g^0 / V_{cat}$ – space velocity, h^{-1} ; $V_{cat} = L \cdot b \cdot h$ – geometric catalyst volume, m^3 ; L , b , h – geometrical dimensions of monolith catalyst, m; V_g^0 – inlet flow rate, Nm^3/s .

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