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Catalytic Reduction of NO and NO_x Content in Tobacco Smoke*

by

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SUMMARY

In order to reduce the nitric oxide (NO) and nitrogen oxides (NO_x) content in mainstream tobacco smoke, a new class of catalyst based on Cu-ZSM-5 zeolite has been synthesized. The effectiveness of the new catalyst (degree of reduction and specific catalytic ability) was tested both by adding Cu-ZSM-5 zeolite directly to the tobacco blend and by addition to the filter. We have determined that adding the catalyst to the tobacco blend does not cause any changes in the physical, chemical or organoleptic properties of the cigarette blend. But, the addition reduces the yield of nitrogen oxides while having no influence on nicotine and "tar" content in the tobacco smoke of the modified blend. The catalyst addition increases the static burning rate (SBR). The changes in the quantity of NO and NO_x may be explained by changes in burning conditions due to the increase of O_2 obtained from catalytic degradation of NO and NO_x, and adsorptive and diffusive properties of the catalyst. The changes in mainstream smoke analytes are also given on a puff-by-puff basis. [Beitr. Tabakforsch. Int. 20 (2002) 43–48]

ZUSAMMENFASSUNG

Um den Gehalt an Stickstoffmonoxid (NO) und Stickstoffoxiden (NO_x) im Hauptstromrauch (HSR) von Cigaretten zu verringern, wurde eine neue Klasse eines auf Cu-ZSM-5 Zeolith basierenden Katalysators synthetisiert. Die Effektivität dieses neuen Katalysators (Ausmaß der Reduzierung und spezifische katalytische Eigenschaften) wurde durch direkte Zugabe des Cu-ZSM-5 Zeoliths zur Tabakmischung und durch Hinzufügen zum Filter getestet. Wir konnten feststellen, dass die Zugabe des Katalysators zur Tabakmischung keine Veränderungen der physikalischen, chemischen und organoleptischen Eigenschaften der Cigarettenmischung hervorrief. Das Hinzufügen des Katalysators verringerte den Gehalt an Stickstoffoxiden, hatte jedoch keinen Einfluß auf den Nikotingehalt und den Gehalt an nikotinfreiem Trockenkondensat im Tabakrauch. Die Zugabe des Katalysators erhöhte auch die statische Abbrandrate (SBR). Die Veränderungen des Gehalts an NO und NO_x können durch veränderte Brennbedingungen erklärt werden, die durch eine Erhöhung des Sauerstoffgehalts nach katalytischem Abbau von NO und NO_x hervorgerufen wurden sowie durch adsorptive und diffusive Eigenschaften des Katalysators. Die Veränderungen der wichtigsten Rauchparameter werden auf zugweiser Basis bestimmt. [Beitr. Tabakforsch. Int. 20 (2002) 43–48]

RESUME

Pour réduire la teneur en monoxyde d'azote (NO) et en oxydes d'azote (NO_x) dans la fumée du courant principal, une nouvelle catégorie de catalyseurs à base du zéolite Cu-ZSM-5 a été synthétisée. L'efficacité du nouveau catalyseur (degré de réduction et capacité catalytique) a été testée en ajoutant le zéolite Cu-ZSM-5 directement sur le mélange de tabac ou sur le filtre. Nous avons déterminé que l'apport du catalyseur au mélange de tabac ne produit pas de changements dans les caractéristiques physiques, chimiques ou organoleptiques du mélange de tabac. Cependant, l'application réduit le rendement en oxydes d'azote mais n'a pas d'influence sur la teneur en nicotine et goudrons dans la fumée du mélange modifié. L'application du catalyseur augmente la vitesse de la combustion statique (SBR). Les changements dans la teneur en NO et NO_x peuvent être expliqués par les conditions de combustion dues à la concentration accrue d'oxygène provenant de la décomposition catalytique de NO et NO_x et des propriétés d'adsorption et de diffusion du catalyseur. Les changements dans la teneur en analytes dans la fumée du courant principal par bouffée individuelle sont également présentés. [Beitr. Tabakforsch. Int. 20 (2002) 43–48]

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Table 1. The main physical-chemical properties of the tested catalyst Cu-ZSM-5

Physical-chemical property	Value
Degree of crystallity (%)	99
Mole ratio SiO_2/Al_2O_3 (%)	95
Degree of ionic exchange (%)	100
Average particle size $d_{o,50}$ (μm)	1.5
Surface area (m^2/g)	425

INTRODUCTION

The existence of nitrogen oxides (NO_x) in tobacco smoke was confirmed in 1959 (1). Since then, many papers have been published dealing with the determination of nitric oxide (NO) and nitrogen dioxide (NO_2) content in smoke. Reported quantities of NO are in the range of 255 to 283 μg/cig while for NO_2 the range is 15 to 99.4 μg/cig (1,2). To some degree, the great differences in reported smoke content of NO and NO_x may be the result of the smoking method or analytical determination. Until now, the best known and applied methods for NO and NO_x reduction in cigarette smoke are filtration and ventilation (3–7).
We have found no literature references on NO and NO_x reduction in tobacco smoke through the use of a catalyst. The possibility of catalytic degradation of NO and NO_x to N_2 and O_2 with a zeolite type catalyst (Cu-ZSM-5) was reported in the work of IWAMOTO (8). The possibility of NO reduction in propane and NH_3 with the zeolite type Cu-ZSM-5 has been shown by SAZONOVA *et al.* (9).
With this knowledge in mind, we wanted to examine the possibility of catalytic reduction of NO and NO_x in tobacco smoke on the zeolite catalyst Cu-ZSM-5.

MATERIALS AND METHODS

Preparation of the catalyst

The catalyst Cu-ZSM-5 zeolite was obtained by the ion-exchange method from a solution of $Cu(CH_3COO)_2$ and Na-ZSM-5 powder. The detailed procedure is described in the work of ADNADJEVIC (10) and the ion-exchange procedure is found in the work of ADNADJEVIC and GAJINOV (11). The main physical-chemical properties of the tested zeolite catalyst are shown in Table 1. At the moment the catalyst is not commercially available and is only synthesized for investigation purpose. It is estimated that the use of the catalyst would increase the production price of cigarettes by about 1%.

Preparation of cigarette samples

As a control material, a prepared tobacco blend for one cigarette brand was taken from the production program of the Tobacco Factory Niš. The catalyst was added to the tobacco blend as a suspension, at a level of 0.1%. Propylene glycol (purum) produced by KUBA, Vienna, and 95% pure ethanol (purum) produced by Crvenka, Yugoslavia, were used for preparing the suspension.

Preparation of the BL cigarette

While mixing the tobacco blend constantly, we added 2% of propylene glycol and 1% of ethanol by spraying. Samples prepared in this way were left for 3 h at room temperature, packed in nylon bags in order to equilibrate. After that period, the tobacco blend was put directly into the hopper of a "PROTOS" type cigarette making machine. The following manufacturing supplies were used for making the cigarette: Filter rod, 120 mm long, made of acetate tow, 2,1Y/42000 with nonporous plug wrap, produced by DIN NIŠ; acetate tow, produced by Celanese; non-porous tipping paper, produced by Cartiera Rossi SpA, Italy; porous cigarette paper with the ventilation of 40 ± 2.5 CORESTA (Cooperation Center for Scientific Research Relative to Tobacco) units, produced by Schoeller & Hoesch, Germany; filter length of the cigarette was 20 mm, tipping paper length was 24 mm. The whole cigarette length was 84 mm. The cigarette BL does not contain a catalyst, so it is the control cigarette on the basis of which all other cigarettes were compared.

Preparation of the BLD cigarette

The tobacco blend for making the BLD cigarette is the following: As much as 96.9% of the tobacco blend in the cigarette comes from the production of DIN NIŠ. One mg/cig is catalyst Cu-ZSM-5, 2% is propylene glycol and 1% is ethanol. Out of this modified tobacco blend and after equilibration, the cigarettes were made in the same way and on the same machine as the cigarette BL.

Preparation of the BLF cigarette

In the BLF cigarette, the catalyst was placed in the filter. Impregnation of acetate fiber was done by adding an adequate quantity of catalyst with triacetin during filter forming.

Methods of testing the chemical composition of the tobacco blend

In order to test the basic chemical composition of the tobacco blend, cigarettes were randomly chosen from the total quantity of finished cigarettes (3000 cigarettes). The cigarettes were conditioned in a dryer under standard conditions, and then, the tobacco was taken from the cigarette tube and finely ground. Moisture of the ground tobacco was determined according to ISO (International Organization for Standardization) 287. Determination of nitrogen, protein nitrogen and soluble sugars was done by the Kjeldahl colorimetric method according to CORESTA Standard No. 37. Tobacco nicotine was determined spectrophotometrically according to ISO 2881. Sand was determined according to ISO 2817, and ash was quantified gravimetrically according to the Yugoslav Standard JUS E.P.3.117. Measurement of pH values was done from a water extract according to JUS E.P.116.

Methods of testing cigarette physical parameters

Before the physical parameters analyses, cigarettes were conditioned for 48 h at the temperature of 22 ± 2 °C and at

Table 2. Chemical analysis of cigarette tobacco blend

Cigarette	Nicotine (%)	Total nitrogen (%)	Protein nitrogen (%)	Proteins (%)	Soluble sugars (%)	Ash (%)	Sand (%)	pH
BL	1.03	2.75	1.55	9.69	16.2	15.47	2.26	5.53
BLD	1.03	2.73	1.54	9.62	16.0	15.40	2.27	5.52
BLF	1.03	2.74	1.56	9.70	16.1	15.49	2.25	5.54

the R.H. of 60 ± 5% according to ISO 3402. Measurement of cigarette weight, draw resistance (puff), caliber and hardness, selected according to previously given parameters as well as statistical processing of results, were done on a SODIMAT apparatus (Société de Diffusion d'Appareils de Mesure, France). Draw resistance measuring was done according to ISO Method 6565.

Methods of testing the organoleptic characteristics of cigarette smoke

Testing of cigarette smoking characteristics was done by a four-member smoking panel according to the methodology of engineer Nikola Sozonovic used in the Tobacco Factory Niš. Three samples of conditioned cigarettes, which were previously selected in accordance with their physical characteristics, were tested. Along with the samples, the smoking panel was also given the cigarette's chemical composition. The results of the smoking panel estimation were interpreted on the basis of the average value of all smoking panel members' estimates per each particular characteristic as well as a total number of points.

Method for determination of the static burning rate

For measuring the static burning rate (SBR), 57 mm of the tobacco rod is combusted for 10 cigarettes without puffs. Measurement of SBR was done by a device produced by Sodim.

Methods of testing chemical composition of the mainstream tobacco smoke

Smoking of cigarettes was performed with an automatic smoking machine, Heinr. Borgwaldt Model RM 20/CS, according to CORESTA No. 22. Twenty cigarettes were smoked at a time with a puff volume of 35 ± 0.3 mL, puffs duration of 2 ± 0.03 s, and a puff interval of 58 s to a 28 mm butt length. Particulate matter (TPM) from tobacco smoke was collected on a Cambridge filter in accordance with ISO 4387. The gas phase was collected in bags. The quantity of raw and dry condensate was determined according to CORESTA No. 10. Nicotine was determined according to CORESTA Standard No. 12, and water in smoke condensate was measured according to ISO Method 10362-2.

Methods of testing the amount of NO and NO_x in the tobacco smoke gas phase

One-way valve connectors were installed on the bags for collecting the gas phase from the tobacco smoke, and then the bags were evacuated by connecting to the vacuum pump. The gas phase of the tobacco smoke was filtered through a Cambridge pad and passed through a one-way valve located on the puffing cylinder of the smoking machine into previously evacuated bags provided for gas samples. Nitric oxide and the mixture of nitrogen oxides were determined by a chemiluminescence method with a chemiluminescence NO_x analyzer, Model 2108, manufactured by DASIBI Environmental Corp.

The mainstream smoke content of NO and NO_x, per cigarette, was measured in the gas phase of 40 cigarettes smoked under standard conditions. Determination of the degree of catalytic reduction (DCR) of NO and NO_x was done according to Equation [1]:

$$\text{DCR (\%)} = \frac{C_o - C_i}{C_o} \cdot 100 \qquad [1]$$

and the degree of catalytic activity (SCA) of a particular catalyst is determined according to Equation [2]

$$\text{SCA} = \frac{\text{DCR}}{m} \text{ (\%/mg)} \qquad [2]$$

where

C_o is the content of NO and NO_x in the smoke of the cigarette without catalyst

C_i is the content of NO and NO_x in the smoke of the cigarette with catalyst, and

m is the mass of the catalyst (mg).

RESULTS AND DISCUSSION

Table 2 shows the chemical composition of the tested cigarettes tobacco blend.

Any differences found in Table 2 are within the range of tolerance for the determination method. These results were expected due to the small amount of applied catalyst (0.1%). Adding the catalyst to a tobacco blend does not change anything in the chemical composition of the cigarettes.

Tables 3, 4 and 5 show minimum (Min), maximum (Max), mean values (Mn), standard deviation (SD) and variation coefficient (CV) for three important physical parameters of cigarettes.

While selecting the cigarettes on the SODIMAT apparatus, the same minimum and maximum limits of physical parameters for the BL cigarette were used for all cigarettes. From Tables 3 to 5, it can be seen that there is no signifi-

Table 3. Physical parameters of the BL cigarette

Cigarette BL	Weight (mg)	Draw resistance (mm H_2O)	Caliber (mm)
Mn	1100	130	7.95
Min	1050	120	7.93
Max	1150	139	7.99
SD	26	5	0.014
CV	2.3	3	0.17

Table 4. Physical parameters of the BLD cigarette

Cigarette BLD	Weight (mg)	Draw resistance (mm H_2O)	Caliber (mm)
Mn	1101	131	7.95
Min	1051	122	7.93
Max	1150	140	7.99
SD	27	5	0.015
CV	2.4	3	0.19

Table 5. Physical parameters of the BLF cigarette

Cigarette BLF	Weight (mg)	Draw resistance (mm H_2O)	Caliber (mm)
Mn	1090	133	7.95
Min	1050	122	7.93
Max	1149	140	7.99
SD	25	4	0.013
CV	2.3	3	0.17

cant difference in cigarette weights because all of them were made on a modern cigarette making machine that automatically corrects cigarette weight during the cigarette making process. There is no meaningful difference in draw resistance among the cigarettes BLD, BLF and BL.

Caliber is the diameter of a cigarette. It was equivalent for all cigarettes because it is a parameter defined and maintained by the cigarette making machine.

Although the chemical and physical properties of the test cigarettes were not changed by adding the catalyst, an increase of the SBR was observed for the BLD cigarette. This increase was 5.3% and 17.3% calculated in mg/cig and mm/cig, respectively (Table 6). For the BLD cigarette these could be explained by the presence of a greater quantity of O_2 in the burning zone as the consequence of NO and NO_x catalytic decomposition (on Cu-ZSM-5 zeolite) to N_2 and O_2 (11).

The contents of RC, DC, nicotine and "tar" (TPM-nicotine) are lower in the smoke of the cigarettes with catalyst compared to the control (Table 7). That decrease is higher for the BLF cigarette and is not proportional to the quantity of catalyst added.

Table 6. Changes in stationary burning rate (SBR) due to catalyst addition

Cigarette	Initial weight (g)	SBR (mg/min)	SBR (mm/min)
BL	7.930	56	4.7
BLD	7.480	59	5.5
BLF	7.940	55	4.7

Table 7. Chemical analysis of tobacco smoke

Cigarette	Nicotine (mg/cig)	"Tar" (mg/cig)
BL	0.72	13.26
BLD	0.70	12.96
BLF	0.68	12.88

It may be seen (Table 7) that there is no significant difference in nicotine and "tar" content among the cigarettes.

These findings, together with the previously observed decrease of RC, DC, nicotine and "tar", could be due to changes in the burning conditions (enrichment in O_2 content and more complete burning). The confirmation for this hypotheses could be found in a reduced content of NO and NO_x (Table 8) in the smoke of the cigarette with catalyst.

The degree of catalytic reduction of NO is higher for the BLF than the BLD cigarette and the opposite result is found in the case of NO_x reduction (19.1%). SCA for the catalyst applied in the filter is significantly lower than SCA of the catalyst added to the blend. The decrease of SCA for the catalyst in the BLF cigarette could be explained by the lower temperature where the catalytic action takes place.

Taking into consideration puff-by-puff measurements (Table 9), we can see that quantities of NO and NO_x increase with puff number whether the catalyst has been added to a cigarette, or not. Also, DCR of NO and NO_x for the BLF cigarette decrease continually with puff number. The same trend is found for the SCA value.

For the BLD cigarette, a rapid decrease of DCR after the fourth and fifth puff was observed. That change, and the NO and NO_x increase with number of puffs could be the result of: a) a constant increase of NO and NO_x in the smoke; b) an increase of reducing compounds content; c) a shorter period of contact between tobacco smoke components and the catalyst; or d) a diminishing of catalyst quantity that is in contact with smoke.

But for the BLF cigarette, a slight increase of NO and NO_x with puff number is detected and could be explained by the increase of NO and NO_x concentration in smoke found for the control cigarette, as the result of pyrolysis, and with a decrease of specific catalytic activity.

From Table 10, it may be seen that all samples of tested cigarettes have approximately the same average estimation of smoking characteristics.

Table 8. Change of NO and NO_x content in the gas phase of tobacco smoke (DCR = degree of catalytic reduction, SCA = specific catalytic activity)

Cigarette	Content NO × 10^6 (mL/cig)	Content NO_x x 10^6 (mL/cig)	DCR_{NO} (%)	DCR_{NOx} (%)	SCA_{NO} (%/mg)	SCA_{NOx} (%/mg)
BL	144.2	383.8	—	—	—	—
BLD	90.7	322.4	37.1	16.0	37.1	16.0
BLF	63.2	334.2	56.2	12.9	11.2	2.6

Table 9. Results of NO and NO_x per puffs (20 cigarettes smoked)

Cigarette	Puff	Content NO × 10^6 (mL/cig)	Content NO_x × 10^6 (mL/cig)	DCR_{NO}	DCR_{NOx}	SCA_{NO}	SCA_{NOx}
BL	(1+2)	43.8	85.3	—	—	—	—
	(4+5)	47.6	90.8	—	—	—	—
	(7+8)	48.8	92.5	—	—	—	—
BLD	(1+2)	8.8	31.2	80.0	63.4	—	—
	(4+5)	35.7	82.5	25.0	9.1	—	—
	(7+8)	43.9	92.5	10.0	—	—	—
BLF	(1+2)	17.5	72.5	60.0	15	12.0	3.0
	(4+5)	20.9	79.0	56.0	13	11.2	2.6
	(7+8)	23.4	82.3	52.0	11	10.4	2.2

Table 10. Average estimation of smoking characteristics of tested cigarettes

Cigarette	Softness of taste	Quality of taste	Quality of flavor	Intensity of flavor	Strength	Combust.	Fullness of smoking
BL	8	7.75	7.25	7.00	7.75	7.75	7
BLD	8	7.62	7.25	7.12	7.75	7.88	7
BLF	8	7.62	7.25	7.12	7.75	7.88	7

The taste of the smoke is soft, and the quality of the taste is medium fine to fine. The quality of flavor in all samples is medium fine and uniform, and the flavor intensity is a bit more stressed in cigarettes with catalyst addition. The strength of cigarette smoke is uniform and ranges from moderately strong to light. Combustibility is better in cigarettes with zeolite catalyst addition, and it is estimated to be “excellent”. All tested cigarettes have “medium full smoking to full smoking” characteristics.

Results of the smoking panel evaluations indicate that adding the catalyst has no influence on the organoleptic characteristics of the cigarette smoke.

CONCLUSIONS

In this study, the catalytic decomposition of NO and NO_x from the mainstream of cigarette smoke, has been examined. On the basis of testing results, the following conclusions may be drawn:

a) Adding a catalyst to the tobacco blend, does not lead to any change in chemical composition of the burning material. This addition does not make changes in nicotine content, pH, or soluble sugars. Sand content is increased in cigarettes with a catalyst in tobacco because chemical composition of Cu-ZSM-5 is aluminum silicate, i.e., sand.

b) Adding the catalyst to the tobacco blend of cigarette or the filter does not change thephysical characteristics of cigarettes.

c) Cigarettes with catalyst added to the tobacco blend have a faster stationary burning rate (SBR), of approximately 16.4%.

d) Adding catalyst Cu-ZSM-5 to the cigarette filter is the most efficient means to eliminate NO from the mainstream smoke. For reduction of the other nitrogen oxides from cigarette smoke, Cu-ZSM-5 added to cigarette tobacco blend proved the best methodology.

e) Smoking panel results show that addition of the catalyst to the tobacco blend has no influence on organoleptic characteristics of the cigarette smoke. Adding even a small amount of catalyst improves cigarette quality, i.e., contributes to "more pure smoking".

f) The results of this study show that catalysts based on zeolite Cu-ZSM-5 can be successfully used for catalytic decomposition of NO and NO_x in mainstream cigarette smoke, and the best results have been achieved by adding Cu-ZSM-5 to cigarette filter.

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