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The influence of the modification of carbonaceous materials on their catalytic properties in SCR-NH_3. A short review

L'influence de la modification des matières carbonées sur leurs propriétés catalytiques dans la réaction catalytique sélective par NH_3. Un bref aperçu

Bogdan Samojeden [*], Monika Motak, Teresa Grzybek

AGH University of Science and Technology, Faculty of Energy and Fuels, al. A. Mickiewicza 30, 30-059 Kraków, Poland

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A B S T R A C T

Carbonaceous catalysts are promising materials for the low-temperature (< 523 K) process of NO reduction with ammonia. Based on literature and own experience of the authors, this review focuses on the possibilities to enhance their catalytic performance. It may be increased by the introduction of oxygen or nitrogen functionalities. So obtained materials may be used in SCR-NH_3 either as catalysts or supports for transition metals oxides/hydroxides. Oxygen functionalities increase activity only to a small extent, but are necessary to prepare an efficient MeO_x/AC catalyst. Nitrogen surface species lead to a considerable increase in $DeNO_x$ activity, as well as stability towards their oxidation to CO_2. As the most efficient active components, oxides of V, Mn, Fe and Cu were found. H_2O leads to the decrease of activity but for some catalysts additionally to the increase in selectivity. The understanding of SO_2 influence needs more experimental data. There still are several open questions concerning more detailed mechanistic studies, and especially the role of nitrogen functionalities, H_2O and SO_2.

R É S U M É

Mots clés :
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SO_2

Les catalyseurs carbonés sont des matériaux prometteurs pour les processus de réduction de NO dans l'ammoniac à basses températures (< 523 K). Le présent article a trait aux possibilités d'amélioration de leur performance catalytique. Celle-ci peut être augmentée par l'introduction des fonctionnalités de l'oxygène ou de l'azote. Les matériaux ainsi obtenus peuvent être utilisés dans la réaction catalytique sélective par NH_3 à la fois comme catalyseurs et comme supports pour les oxydes/hydroxydes de métaux de transition. Les fonctionnalités de l'oxygène n'augmentent l'activité que dans une faible mesure seulement, mais ils sont indispensables pour préparer un catalyseur MeO_x/AC efficace. L'azote en surface conduit à une augmentation considérable de l'activité de $DeNO_x$, ainsi qu'à une meilleure stabilité face à l'oxydation en CO_2. Ce sont les oxydes de V, Mn, Fe et Cu qui se sont avérés être les composants actifs les plus efficaces. Des méthodes de préparation des monolithes carbonés ou en carbone–céramique ont été proposées. H_2O

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[*] Corresponding author.
E-mail address: bogdan.samojeden@agh.edu.pl (B. Samojeden).

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conduit à une diminution de l'activité mais, pour certains catalyseurs, conduit en outre à l'augmentation de la sélectivité. L'appréhension de l'influence de SO_2 nécessite davantage de données expérimentales. Cependant, plusieurs questions restent ouvertes concernant des études mécanistiques plus détaillées, et en particulier le rôle des molécules d'H_2O et SO_2 et des fonctionnalités de l'azote.

1. Introduction

EU directive 2010/75/EU [1] requires the drastic reduction of NO_x emission in flue gases from the 1st of January 2016. Until now the norms could have been fulfilled in many cases with appropriate primary measures, such as e.g., flue gas recirculation, air staging, low excess air technique, low NO_x burners, etc. The BAT methods for coal fired power stations, allowing the fulfilment of the new norms, require now (with the exception of fluidized bed combustion) that either selective non-catalytic reduction SNCR or selective catalytic reduction SCR be introduced in large stationary sources. Selective catalytic reduction (SCR) of NO_x with ammonia is the most efficient method of NO_x emissions reduction and it is widely used in EU, USA and Japan.

The requirements for in SCR-NH_3 are as follows: a catalyst should:

- be active in reduction of NO_x in the oxidizing atmosphere and not sensitive to the changes in oxygen content (flue gases usually contain ca. 6% O_2);
- have a good selectivity to N_2 and not lead to a side product N_2O, as it is a greenhouse gas ca. 300 times more harmful then CO_2;
- be stable, i.e. not undergo structural or chemical changes under operation conditions;
- have low activity towards oxidation of ammonia, especially to dinitrogen oxide;
- have a broad temperature window;
- not deactivate with H_2O, which is always present in flue gases;
- be resistant towards typical poisons present in flue gases, especially SO_2.

Additionally, it would be of advantage if the catalysts could be installed at end-tail configuration where the flue gas has already been cleaned of fly ash and most of sulfur dioxide.

A catalyst most often applied in industry applied catalyst is a monolith with vanadium as active component and titanium as a support with the addition of tungsten oxide or molybdenum oxide promoter to increase the catalyst lifetime by decreasing the harmful influence of sulfur oxides. The temperature window of such catalysts is fairly broad in comparison to e.g., Pt-containing catalysts, but optimum operation temperature is from ca. 573 K to 673 K. This catalyst may be installed either (i) upstream of the electrostatic precipitator (ESP) or (ii) downstream of the ESP and upstream of the desulfurization unit (FGD). In the former case, its life may be shortened by fly ash and sulfur dioxide, and in the latter one by SO_2. The operation of SCR downstream of FGD unit requires the reheating of flue gas. This is the main reason why low-temperature catalysts (below 523 K) are searched. Among the best candidates are carbonaceous materials, which, in contrast to V_2O_5/TiO_2 systems, are active at temperature as low as 393 K. Moreover, it was found in many cases that the same active component showed higher NO conversion when supported on active carbon than on Al_2O_3 or TiO_2 [2,3]. There are examples in the literature showing that V_2O_5/carbonaceous materials are more active than commercial $V_2O_5/WO_3/TiO_2$ [4]. Actually, there exists a $DeSO_x$–$DeNO_x$ technology based on activated carbons–BF-Mitsui technology [5,6] which is considered a BAT method under appropriate circumstances. In this method, SO_2 is removed from flue gases by adsorption on activated carbon, and NO_x are reduced with ammonia, but, due to insufficient activity of carbonaceous materials, the technology has to apply moving beds. It was observed, however, that different types of modification might result in considerable increase in NO conversion.

The main focus of this work is to discuss, based on published literature and the own results of the authors, the possibilities to enhance the catalytic performance of carbonaceous catalysts and to shed light both on the possible preparation procedures, and open questions concerning the design of successful carbonaceous catalysts. Special attention has been paid to carbons containing oxygen and/or nitrogen surface functionalities, used both as catalysts and as supports for active components.

2. The possibilities of the modification of carbon materials

Carbon materials, especially activated carbons and carbon fibres, are characterized by their textural, as well as chemical and surface properties. They are very important both for adsorption and catalysis but S_{BET} may not always be correlated with catalytic performance. It was recognized that for carbon materials, the decisive role was played by surface chemistry [7,8]. The change in surface chemistry affects adsorption and catalytic properties of the modified carbonaceous materials. Figueiredo and Pereira [7] gave an overview of the reactions catalyzed by carbon materials, together with the type of sites necessary for these processes. Among the reactions important for environmental protection, the following should be mentioned: selective catalytic reduction of NO_x with NH_3, for which acidic and basic sites are of importance, NO reduction with propene [9], NO or N_2O reduction by carbon [10], oxidation of NO, SO_2 or H_2S [7], which require basic sites, or hydrodehalogenation where pyridinic nitrogen sites were identified as being of primary