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ScienceDirect
Catalysis Today 119 (2007) 152–155
CATALYSIS TODAY
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Role of redox and acidic properties of $CoO/ZrO_2(SO_4^{2-})$ catalysts in CH_4-SCR of NO

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Available online 20 September 2006

Abstract

The activity of cobalt-containing catalysts based on sulfated zirconium dioxide in selective catalytic reduction of NO by methane depends on the amount of sulfur and the preparation method. Modification by Fe and Mn improves the catalytic behavior of SO_4^{2-}/ZrO_2 as a result of the increase in the concentration of active sites. The SCR-activity of the oxide catalysts based on zirconium dioxide depends on the chemical nature and strength of redox and acid centers of the catalysts.

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Keywords: Nitrogen monoxide; Reduction; Methane; Sulfated zirconium dioxide; Transition metal oxides; Acidity; Bifunctionality

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1. Introduction

Selective catalytic reduction of nitrogen oxides by hydrocarbons (the SCR process), being one of the most highly studied processes, requires selection of new systems satisfying the requirements imposed on gas purification catalysts. Active zeolite catalysts for the SCR process have acid sites in addition to the active sites capable of participating in the oxidation–reduction cycle [1,2]. Pietrogiacomi et al. [3] and Delahay et al. [4] have discussed the properties of oxide catalysts for the SCR process based on zirconium dioxide modified by transition metals (Cu and Mn). These catalysts display SCR activity specifically due to the acid properties of sulfated zirconium dioxide and the oxidation–reduction properties of the transition metal. Sulfated zirconium dioxide (SO_4^{2-}/ZrO_2) which as a solid superacid, has attracted steady attention of researchers [5]. (The question concerning whether sulfated zirconium dioxide is definitely a superacid has not yet been answered, and is the subject of discussion [6].) In order to obtain SO_4^{2-}/ZrO_2 having special acid properties, we need to consider a number of factors such as the nature of precursors of the zirconium dioxide and the sulfate ion, concentration and oxidation state of sulfur on the oxide surface, the calcination temperature for the system, etc. [5]. A characteristic feature of the systems based on sulfated zirconium dioxide is low sensitivity to the action of water vapor and sulfur dioxide, and also high regeneration capacity of the catalysts after removal of SO_2 from the reaction mixture [7,8]. It is shown in Ref. [7] that when a number of transition metals (Co, Mn, Ni) are added to a specimen of SO_4^{2-}/ZrO_2 that displays low activity in selective catalytic reduction of NO by methane, we observe an increase in NO conversion up to 60%.

We have studied the catalytic and acid properties of differently prepared zirconium dioxide impregnated with variable-valence metal oxides (Cr, Co, Ce) by the temperature programmed desorption of ammonia (NH_3-TPD) and IR spectroscopy and we have shown that the SCR activity of M_xO_y/ZrO_2 systems correlates with the acid properties of their surface. The more active catalysts have strong Brønsted acid sites [9].

In the present work, we studied the effect of synthesis conditions and amount of sulfate ions on the catalytic properties of sulfated zirconium dioxide modified by cobalt, iron, and manganese oxides in selective catalytic reduction of NO by methane.

2. Experimental

2.1. Preparation of catalysts

Zirconium dioxide was prepared by precipitation. Zirconium hydroxide was precipitated from a stirred aqueous

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doi:10.1016/j.cattod.2006.08.033

solution of zirconium oxochloride with 2.5 M solution of ammonia at the temperature 20 °C and constant pH 9. $Zr(OH)_4$ was aged in the mother liquor for 5 days, washed with aqueous ammonia (pH 8) until a negative reaction for Cl^- ions, and dried at the temperature of 170 °C for 3–4 h. It follows from XRD data that the monoclinic modification of zirconium dioxide ($2\theta = 28.43^\circ$ and 31.71°) is formed upon thermal treatment of $Zr(OH)_4$ at 460 °C.

The methods for obtaining sulfated zirconium oxide described in the literature include: impregnation of zirconium hydroxides with sulfur compounds (sulfuric acid, sulfates, sulfides, persulfates, sulfuric acid esters, etc.) followed by calcination at 600–650 °C [10]; decomposition of zirconium sulfates at 725 °C [11]; and a one-step synthesis using the sol–gel method [12]. We selected the first one since, according to [10], only H_2SO_4 and $(NH_4)_2SO_4$ can form superacid sites, while other sulfur compounds listed above do not have an effect on the acidity.

The sulfur was applied in amounts of 0.5–3 wt.% by impregnation of previously synthesized xerogel of zirconium hydroxide with sulfuric acid solutions.

Catalysts were prepared by the impregnation of $ZrO_2(SO_4^{2-})$ with solutions of cobalt nitrate followed by drying at 100 °C and calcination at 320 °C for 6 h. The catalysts of the composition $CoO/ZrO_2(SO_4^{2-})$ containing 10 wt.% of cobalt oxide on the support (calculated on the basis of the metal) were prepared. The cobalt-containing samples (SO_4^{2-}/ZrO_2) obtained were modified by iron and manganese (1.5 and 0.5 wt.%, respectively). The metals were introduced by impregnation with iron nitrate and manganese acetate solutions.

2.2. *Characterisation*

The acidic properties of the catalyst surface were studied by NH_3-TPD and IR spectroscopy according to the following procedures. Samples with grains of 1–2 mm (0.2 g) were loaded into a flow quartz reactor ($d = 0.6$ cm) and treated in a helium flow ($v = 60\,\text{ml/min}$) for 1 h at 700 °C. After the temperature was decreased to 100 °C, the sample was saturated with ammonia. The completion of saturation was checked by titration with ammonia at the outlet of the reactor. The saturated sample was purged with helium at 100 °C for 30 min to remove physically adsorbed NH_3. Then the sample was subjected to programmed heating in a helium flow with a rate of 26 °C/min. Thermal desorption was monitored with a thermal conductivity detector, and the amount of desorbed ammonia was estimated by titration with HCl.

Thoroughly dried pyridine was adsorbed on the samples, previously evacuated at 550 °C, at a temperature of 150 °C for 20 min, and then the samples were evacuated at the same temperature to remove physically adsorbed pyridine. The IR spectra were recorded on a Specord 75IR spectrophotometer.

2.3. *Activity measurements*

The catalytic activity of the prepared catalysts in the selective catalytic reduction of NO–CH_4/O_2 was characterized by NO conversion to N_2/N_2O. It was measured in a quartz gradientless reactor in 250–500 °C temperature range. The composition of the reaction mixture was (vol.%): 0.05% NO + 0.09% CH_4 + 5% O_2 at the space velocity GHSV = 6000 h^{-1}. The concentration of NO was measured on a 344-KhL-04 gas analyzer with a chemiluminescence detector; other reagens were analyzed by chromatography (a thermal conductivity detector) on CaA molecular sieves (N_2, CO, O_2, CH_4) and polysorb (N_2O, CO_2, H_2O).

3. Results and discussion

3.1. *SCR-activity of $CoO/SO_4^{2-}/ZrO_2$ samples*

The activity of cobalt oxide catalysts ($CoO/SO_4^{2-}/ZrO_2$) in selective catalytic reduction of NO by methane depends on the amount of sulfate ions applied (Table 1, Fig. 1). The maximum conversion of nitrogen monoxide to nitrogen was 26% at 360 °C for the specimen containing the minimal amount (0.5 wt.%) of sulfur. According to literature data [4,5], the most active catalysts are those in which the sulfur concentration corresponds to approximately a monolayer coating on the ZrO_2 surface with SO_4^{2-} anions.

Introducing iron and manganese in the above-indicated amounts into 10% $CoO/SO_4^{2-}/ZrO_2$ (2% and 0.5% S) specimens promotes increasing activity of the studied reaction: conversion of NO is as high as 48–62% at 350 °C. The promoting effect of iron and manganese on sulfated zirconium dioxide is also observed for other reactions. In particular, in isomerization of *n*-butane the activity of the catalyst increases by three orders of magnitude and deactivation of the system also decreases [13]. The interaction between Co, Fe, Mn and acid sites of the sulfated zirconium dioxide probably leads to

Table 1
Catalytic activity in CH_4-SCR of NO and concentration of acid sites from the data of NH_3-TPD for specimens based on SO_4^{2-}/ZrO_2

Catalyst	NO conversion/*T* at which achieved (°C)	Concentration of acid sites (mmol NH_3/g)
SO_4^{2-}/ZrO_2 (0.5% S)	Inactive	0.07
CoO[a]$/SO_4^{2-}/ZrO_2$ (0.5% S)	26/360	0.07
$CoO/SO_4^{2-}/ZrO_2$ (2% S)	20/410	0.07
$CoO/SO_4^{2-}/ZrO_2$ (3% S)	18/410	0.1
CoO(Mn, Fe)$/SO_4^{2-}/ZrO_2$ (0.5% S)	62/350	0.38
CoO(Mn, Fe)$/SO_4^{2-}/ZrO_2$ (2% S)	48/350	0.27

[a] The specimens contained 10 wt.% cobalt.

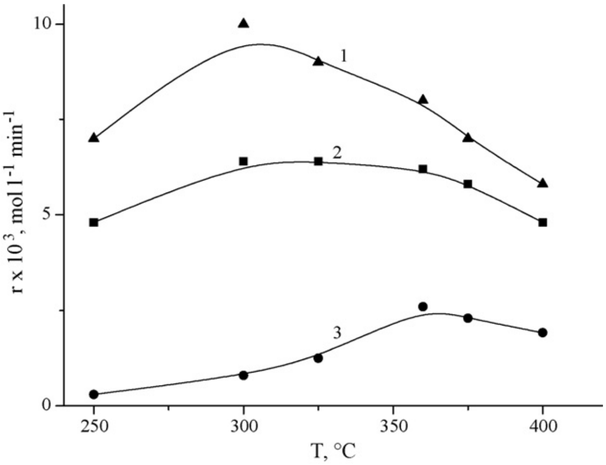

Fig. 1. Temperature dependences of the reaction rate for selective catalytic reduction of NO by methane (0.05% NO + 0.09% CH_4 + 5% O_2; GHSV = 6000 h^{-1}). 1: CoO/ZrO_2 [9]; 2: CoO(Mn, Fe)/SO_4^{2-}/ZrO_2 (0.5% S); 3: 10% $CoO/SO_4^{2-}/ZrO_2$ (0.5% S).

stabilization of the positively charged metal species. Thus Fe^{3+} ions on the SO_4^{2-}/ZrO_2 surface can be readily reduced upon reaction with alkanes and consequently can participate in oxidation–reduction reactions [5]. The role of manganese consists in stabilization of iron in the highly dispersed state [6].

3.2. Acidic properties of $CoO/SO_4^{2-}/ZrO_2$

The activity data (Table 1) are of interest in connection with the acidity of the catalysts determined from the data of thermal desorption of ammonia. The concentration of acid sites for the original SO_4^{2-}/ZrO_2, which does not display activity under the studied conditions, and cobalt-containing specimens is 0.07–0.1 mmol NH_3/g. Introduction the mixture of manganese and iron increases the concentration of acid sites up to 0.27–0.38 mmol NH_3/g and leads to an increase in catalytic activity.

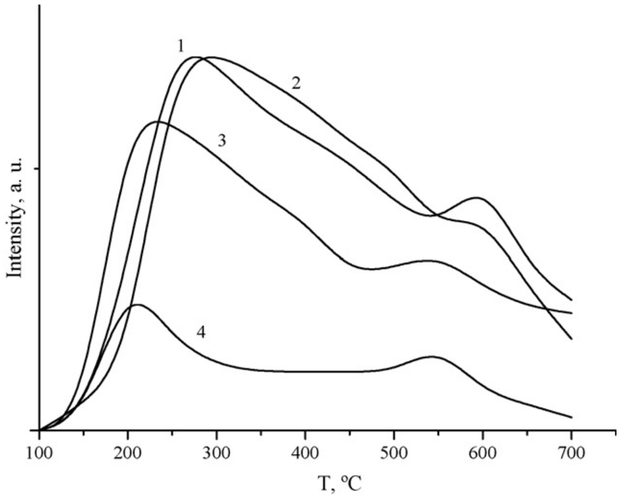

Fig. 2. Temperature programmed desorption of ammonia spectra from the surface of the specimens. 1: $CoO/SO_4^{2-}/ZrO_2$ (0.5% S); 2: $CoO/SO_4^{2-}/ZrO_2$ (3% S); 3: $CoO/SO_4^{2-}/ZrO_2$ (2% S); 4: SO_4^{2-}/ZrO_2 (0.5% S).

The curves of thermal desorption of ammonia for specimens of the original sulfated zirconium dioxide and cobalt-containing catalysts based thereon with different amounts of sulfur are characterized by smeared out peaks at 200–400 °C and small peaks at 500–600 °C (Fig. 2). According to the data in Ref. [5], the NH_3-TPD method does not provide a correct estimate of the strength of acid sites for sulfated zirconium dioxide, since increasing the desorption temperature to 500 °C leads to reaction of surface active sites on SO_4^{2-}/ZrO_2 with the adsorbate and formation of N_2 and SO_2. On the other hand, it was shown in Ref. [14] by using the same method that the sulfated zirconium dioxide has superacid sites, evidence for which comes from the peak on the thermal desorption curve at 540 °C. The results presented above are consistent with data we

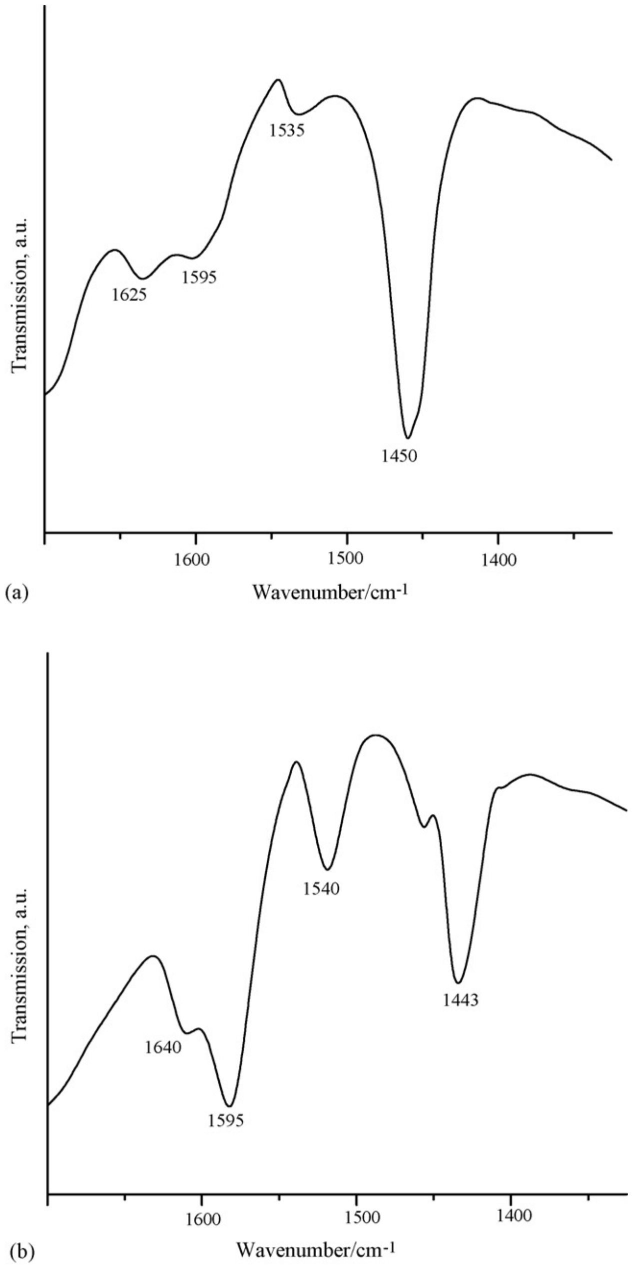

Fig. 3. IR spectra of pyridine adsorbed on 10% $CoO/SO_4^{2-}/ZrO_2$ (0.5% S) (a) and 10% CoO/ZrO_2 (b).

obtained previously in Ref. [9] showing that active oxide catalysts for the SCR process are bifunctional in nature, i.e., are characterized by the presence of an active metal (metal oxide) and a certain acidity of the surface.

In Fig. 3a and b we show the IR spectra for adsorbed pyridine on cobalt-containing sulfated $CoO/SO_4^{2-}/ZrO_2$ (0.5% S) and unsulfated CoO/ZrO_2 catalysts. The absorption bands at 1535–1540 cm^{-1} and 1640 cm^{-1}, typical of the pyridinium ion, suggest the presence of Brønsted acid sites on the surface of the catalysts. Based on the intensity of the absorption bands, the concentration of Brønsted acid sites is higher for the unsulfated specimen. The absorption bands we observed (1595 and 1450 cm^{-1}) for both specimens, according to [15], characterize formation of sorption complexes of pyridine with electron-acceptor sites on the catalyst, i.e., Lewis acid sites. The results obtained are consistent with the data in Ref. [16], where it was established using the diffuse reflection IR spectroscopy that modification of the zirconium dioxide surface with sulfate groups leads to the appearance of a new type of Brønsted acid site. Such sites do not correspond to the superacid properties of SO_4^{2-}/ZrO_2, ensuring in particular isomerization of *n*-butane, since they are weaker in strength than the analogous sites in H-ZSM-5 zeolites. In order to explain this, it has been hypothesized that protons form bonds with oxygen atoms of the crystal lattice and sulfate groups. When cobalt, iron, zinc, or nickel ions are introduced into SO_4^{2-}/ZrO_2, additional Lewis acid sites appear.

The higher activity of the CoO/ZrO_2 specimen in selective catalytic reduction of NO by methane (72% conversion of nitrogen monoxide is achieved at 300 °C [9]) compared with the sulfated specimen $CoO/SO_4^{2-}/ZrO_2$ (0.5% S) may be connected with the higher concentration of Brønsted acid sites on its surface, which is consistent with the results of [17] on the increase of the rate of formation of nitrogen as the number of acid sites increases. In other words, sulfation of zirconium dioxide does not improve the efficiency of cobalt–zirconium oxide systems under the studied reaction conditions.

4. Conclusions

The activity of cobalt-containing catalysts based on sulfated zirconium dioxide under conditions for selective reduction of NO by methane depends on the amount of the introduced sulfate ions: better results are obtained for specimens with the minimal (0.5 wt.%) amount of sulfur. According to IR spectroscopy data, the higher activity of CoO/ZrO_2 compared with specimens based on sulfated zirconium dioxide may be connected with the higher concentration of Brønsted acid sites on the surface of the catalyst. Introduction of iron and manganese improves the catalytic behavior of the sulfated systems as a result of the increase in concentration of active sites (the overall concentration of acid and oxidation–reduction sites).

Thus, the SCR-activity of the oxide catalysts based on zirconium dioxide depends on the chemical nature and strength of redox and acid centers of the catalysts.

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