Cobalt catalysts in selective catalytic reduction of NO by methane

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Impregnated cobalt-containing catalysts are studied in the selective catalytic reduction of NO by methane. The active component of all the impregnated cobalt-containing catalysts is Co_3O_4. The role of O_2 seems to maintain the surface stoichiometry of Co_3O_4. The main reason of decrease of catalytic activity of samples based on MgO, SiO_2, Al_2O_3 in selective catalytic reduction of NO is due to oxide–oxide interaction promoted by water. Catalysts based on montmorillonite (HMM) are stable in the presence of water. All the carriers can be placed by the capability for oxide–oxide interaction in the following order: $SiO_2 \gg MgO > Al_2O_3 \gg HMM$.

Keywords: montmorillonite, selective catalytic reduction of NO, methane, water, role of O_2, oxide–oxide interaction

1. Introduction

Increasing concerns about the air quality and our environment have led to tougher regulations, adopted by many countries of the world, to control exhaust emission of mobile and stationary sources of emission. For the past few years, there has been a growing interest in the use of light hydrocarbons, in place of ammonia, to selectively reduce NO_x in oxidising environment. Methane seems to be the most appropriate reducing agent for NO_x because it is available, cheap, ecologically safe and it is widely used as a fuel for many electrical utilities and stationary combustion engines.

Recently, for the first time, Li and Armor [1,2] reported a family of metal-exchanged zeolites catalysts, which can effectively reduce NO_x with CH_4 in the presence of excess of O_2. At the same time there is little information about the impregnated catalysts in the selective catalytic reduction (SCR) of NO_x by methane. Recently, it has been reported that a number of Co- and Fe-containing impregnated catalysts are rather active in the de-NO_x process [3]. The activity of Fe-containing catalysts depends on the carrier, iron concentration and phase content. This paper focuses on the influence of reaction, preparing and activating conditions on the content and properties of cobalt phase.

2. Experimental

All the samples were prepared by the incipient wetness technique using a cobalt nitrate solution as follows: the sample was wetted by the solution containing the calculated amount of $Co(NO_3)_2$. Then it was dried over the hot water bath under constant mixing. The preparation was dried at 388 K for 3 h and calcined in air at 823 K for 5 h. The carriers were montmorillonite (HMM) (340 m^2/g), MgO (90 m^2/g), Al_2O_3 (150 m^2/g), SiO_2 (190 m^2/g).

The catalytic activities were measured by using a steady-state installation at normal pressure. To reduce pressure drop, the catalyst was pelletised, crushed and then sieved to 0.25–0.1 mm before use. The usual temperature range was 573–973 K, the flow-rate of the feed was 1000 cm^3/min (GHSV $= 40{,}000\ h^{-1}$). The reaction mixture typically consisted of 300 ppm NO, 400 ppm CH_4, 16% O_2 (balance in nitrogen). Gas analyser GIAM-15M was used to measure NO concentration.

The samples surface area was measured by using a standard BET method. Magnetic investigations were carried out at a magnetometer described in [4].

Temperature-programmed reduction (TPR) was performed at a modified installation KL-1 at a temperature ramp rate 0.2 K/s. Gas mixture contained 10% of H_2 in nitrogen. The amount of sample was calculated from conditions described in [5]. Usually it was 40–45 mg. The level of reduction was calculated by the following way:

$$\beta = \frac{\nu_{H_2}}{\nu^0_{H_2}} \times 100\%,$$

where $\nu^0_{H_2}$ is the theoretical amount of hydrogen consumed (mmol), calculated by using metal concentration and ν_{H_2} is the amount of hydrogen consumed (mmol).

NO adsorption was investigated by IR technique by using "SPECORD M80". Electron spectra of diffuse reflectance (ESDR) were taken by using "SPECORD M42". For spectroscopic studies, all the samples were diluted by MgO (1 : 10).

3. Results and discussion

The typical curves of NO conversion versus temperature over cobalt-containing catalysts are presented in figure 1 and in table 1. The activity of all the impregnated systems depends on carrier nature and cobalt concentration. There is maximum of NO conversion at 5–10% of Co concen-

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tration. Further increase of Co loading till 30% does not enhance the activity of the impregnated catalysts. From table 1 one can see that activity depends on cobalt concentration immonotonously. Li and Armor [1,2] have shown that the growth of the number of isolated Co^{2+} ions increases catalytic activity proportionally. Considering well pronounced cation-exchanged properties of montmorillonite we could expect that cobalt is present in such samples both as phase (Co_3O_4) and as isolated ions (Co^{2+}). So, for better understanding of the active component nature, all the samples were studied by the ESDR technique. Electron spectra of 1% Co-HMM contains only one very broad band of $Co_{O_h}^{3+}$ ions at 13,300 cm^{-1} (figure 2). The intensity of this band increases when cobalt amount raises up to 2%. Also, a new broad band at 22,200 cm^{-1} attributed to $Co_{O_h}^{3+}$ ions [6,7] was determined. All these bands must belong to the phase Co_3O_4. The bands of $Co_{T_d}^{2+}$ ions lay at the same frequencies with the bands of montmorillonite, so they cannot be identified. The changes observed in the ESDR spectra are in good agreement with magnetic data. All the samples containing over 2% of cobalt on reducing with H_2 at 673 K were ferromagnetic. The sample 1% Co-HMM was not ferromagnetic on reducing and it was completely inactive (table 1). The growth of cobalt concentration from 2 up to 30% increases the intensity of the bands at 22,200 and 13,300 cm^{-1}, and the intensity of background as the phase Co_3O_4 is not stoichiometric.

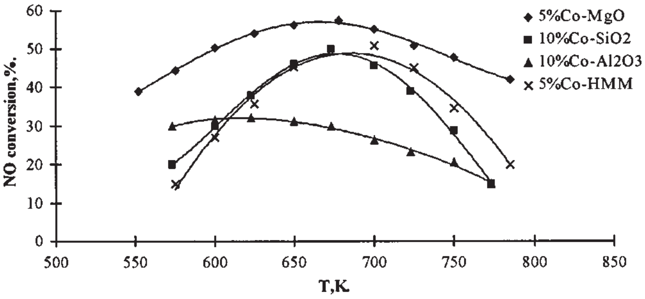

Figure 1. Activity of cobalt-containing catalysts based on different carriers. GHSV = 40,000 h^{-1}.

Table 1
Cobalt concentration influence on the activity of cobalt-containing catalysts based on montmorillonite (HMM).

Catalysts	NO conversion (%)		
	573 K	673 K	773 K
1% Co-HMM	0	0	0
2% Co-HMM	0	15	5
5% Co-HMM	15	50	20
10% Co-HMM	15	45	25
20% Co-HMM	25	45	20
30% Co-HMM	30	45	20
4% Co-HZSM-5	15	40	20

The ESDR spectra of the samples based on MgO and Al_2O_3 consist of the $Co_{O_h}^{3+}$ ions bands at 13,600, 23,100 cm^{-1} and $Co_{T_d}^{2+}$ ions bands at 35,000 cm^{-1}. All these bands were assigned by [6,7] to the bulk-phase Co_3O_4. The presence of the same bands in all the spectra shows that cobalt is present on the surface as Co_3O_4. The phases $CoAl_2O_4$ and $CoMgO_2$ were not detected. So, all the prepared catalysts contain bulk Co_3O_4 on the surface.

To study the influence of phase content on the catalytic properties all the catalysts were reduced by methane

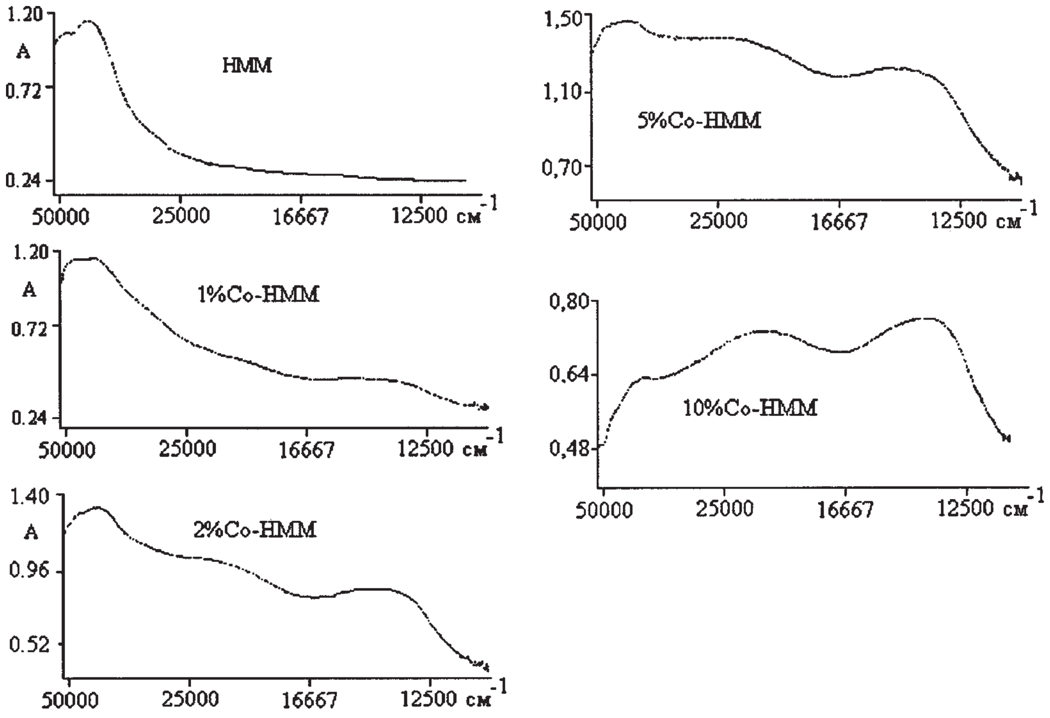

Figure 2. ESDR spectra of cobalt-containing catalysts based on montmorillonite (HMM).

Table 2
Water influence on the level of reduction of cobalt-containing catalysts.

Carrier	Reduction level[a] (%)			
	Initial	0% H_2O	2% H_2O	Activated[b]
SiO_2	100	16	15	–
Al_2O_3	100	90	30	–
MgO	100	60	30	–
Montmorillonite	100	100	90	100

[a] Reduction level was calculated considering that cobalt is present only on Co_3O_4.

[b] Reduction level was calculated considering that cobalt is present only on CoO.

at 803 K for 1 h. Such an activation increases NO conversion over almost all the catalysts except 5% Co–MgO (table 2). But such systems are not stable in the SCR and their activity quickly falls. The changes of NO conversion over 10% Co-HMM after the activation are illustrated in figure 3(a). The TPR measurements detected the changes in phase content in points 1–4 (figure 3(b), curves 1–4). The initial samples contain the only phase Co_3O_4. The activation by methane leads to complete reduction of Co_3O_4 to CoO. This was proved by calculations of H_2 consumption (table 2) and magnetic measurements. The samples reduced by methane were not ferromagnetic at all, i.e., reduction of CoO to Co did not occur.

After activation the maximum activity was registered. After 2 h of the SCR Co_3O_4 appeared. It is very important as despite different amount of CoO in samples 3 and 4 (figure 3(b)), their activity is almost equal. This fact points out that the surfaces of the CoO particles are oxidised very quickly. In 10 min of oxidation of activated catalyst at 673 K in the air, the mono- and di-nitrosyl bands of NO adsorbed on CoO disappear. Only the bands assigned to NO_2 species are observed in IR spectra. Afterwards, the oxidation of bulk CoO takes place. That is why the activities of samples 3 and 4 do not differ greatly.

When NO is reduced, water vapour is always present as a product. H_2O can hydrate the isolated ions; it can adsorb on the active sites of catalysts instead of NO [8]. Besides, it greatly increases oxide–oxide interaction (OOI) between the carrier and the active component [9]. We have discovered that the activity of impregnated catalysts based on MgO, Al_2O_3, SiO_2 irreversibly falls in the presence of 2% of water vapour (figure 4) accompanied by the decrease of the degree of catalysts reduction (table 2). Water promotes the formation of spinels in the samples based on Al_2O_3, solid solutions in the MgO-containing systems and cobalt silicates in the SiO_2-containing systems. X-ray analysis proved the formation of these phases.

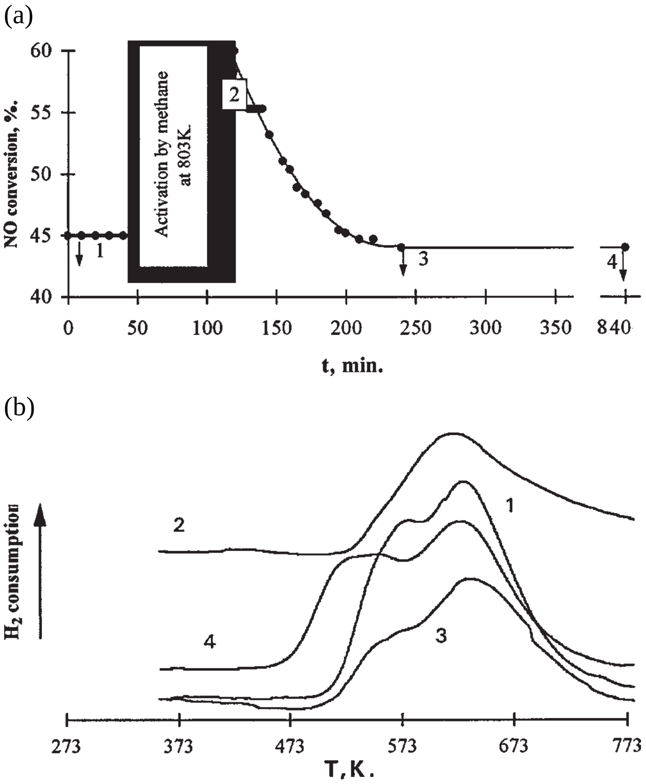

Figure 3. Catalytic activity at 673 K (a), and TPR curves (b) of the catalyst 10% Co-HMM. In points 1–4 (a), the reactor was flushed by nitrogen, cooled till room temperature: 1, initial; 2, activated; 3, after the catalytic test (0% water, 2 h); 4, after the catalytic test (2% water, 14 h).

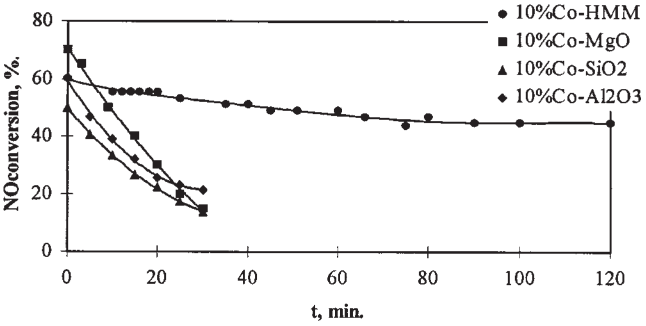

Figure 4. Influence of water vapour (2%) on the NO conversion at 673 K.

Contrary to the other supports, the montmorillonite was the only where the OOI was insignificant in the presence of water. The activity of the catalysts based on montmorillonite slightly falls down after introduction of 2% water vapour in the gas flow and remains constant for at least 14 h (figure 3). The influence of water vapour on the samples based on montmorillonite appeared to be reversible. Such behaviour of montmorillonite is explained in the way that some tetrahedral positions on SiO_2 structure are occupied by Mg^{2+} and Al^{3+} ions as in [10] it is shown that the OOI greatly decreases when K^+ or Mg^{2+} are presented in the tetrahedral positions. So, all the carriers can be placed by the capability for the OOI in the following order: $SiO_2 \gg MgO > Al_2O_3 \gg$ HMM. The activity decrease of catalysts based on MgO, SiO_2, Al_2O_3 in the SCR of NO is due to the OOI. The catalysts based on montmorillonite are stable in the presence of water.

The data obtained allows us to point out some specific feature of the SCR over impregnated catalysts. The principal difference of these catalysts versus ion-exchanged zeolites is in the different active components. In [11], the activity if ion-exchanged zeolites was shown to depend on

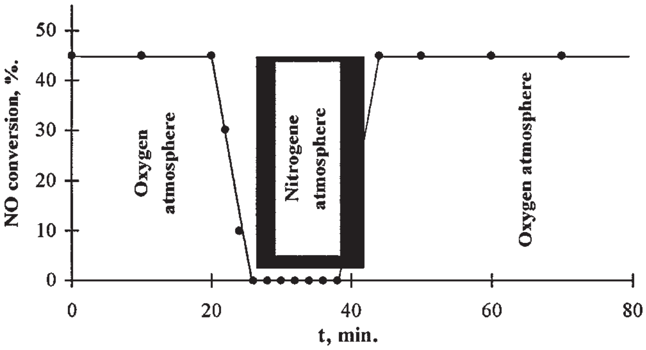

Figure 5. Role of O_2 in the SCR over 10% Co-HMM at 673 K.

isolated Co^{2+} ion concentration. The activity of impregnated catalysts can be attributed to the presence of bulk phase Co_3O_4.

The distinctive feature of Co_3O_4-supported samples in comparison with widely investigating Co-HZSM-5 type SCR catalysts lies in the fact that, despite great difference in the amount of active sites in the ion-exchanged zeolites (Co^{2+}) and Co_3O_4-supported catalysts, their observed activity is comparable (table 1). We suppose that the bulk phase Co_3O_4 is more active than the isolated Co^{2+} ions [12] because of the participation of lattice oxygen of Co_3O_4 in the oxidation of NO and the formation of nitrite–nitrate complexes [13]. These complexes react with methane producing CO_2, H_2O and N_2. After their desorption, oxygen vacancies remain on the surface of Co_3O_4. Oxygen coming from gas phase regenerates the surface stoichiometry. Without oxygen, the SCR of NO is not observed (figure 5) either over initial or activated catalysts. Methane combustion was detected only at the temperature over 773 K. When the temperature is lower than 773 K, no methane combustion was observed over all the catalysts.

References

[1] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L31.
[2] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.
[3] V.V. Lunin, P.A. Chernavsky, P.V. Ryabchenko and I.I. Novochinsky, Russia Patent No. 95118506/04 (032107) (1995).
[4] V.V. Kiselev, P.A. Chernavsky and V.V. Lunin, J. Fiz. Him. 29(3) (1987) 280.
[5] A. Monti and A. Baiker, J. Catal. 83 (1983) 323.
[6] A.E. Cherkashin and F.I. Vilesov, Fiz. Tverd. Tela 11(5) (1969) 1319.
[7] J.H. Ashley and P.C.H. Mitchel, J. Chem. Soc. A(11) (1968) 2821.
[8] Y. Li, P.J. Battavio and J.N. Armor, J. Catal. 142 (1993) 561.
[9] V.V. Lunin and P.A. Chernavsky, Kinet. Katal. 34(3) (1993) 531.
[10] Q. Caixia, B. Tingfang and A. Lidun, React. Kinet. Catal. Lett. 55(1) (1995) 131.
[11] Y. Li and J.N. Armor, Appl. Catal. B 3 (1993) 55.
[12] Y. Li, T.L. Slager and J.N. Armor, J. Catal. (1994) 388.
[13] A.N. Il'ichev, A.A. Ukharsky and V.A. Matyshak, Mendeleev Commun. (1995) 118.