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Chemical Engineering Journal 120 (2006) 107–111

Chemical Engineering Journal

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Spent Pd catalyst—Component for oxide catalysts, designed for CO oxidation and NO reduction

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Abstract

The aim of this investigation is to check the possibility of using, after Pd extraction, the residue of deactivated alumina–palladium catalyst as a component of an oxide composite, as well as to establish the effect of Pd on the catalyst activity. In order to do so, Cu–Co active phase was impregnated on catalyst containing Pd residue (synthesized catalyst 3KN). The polyoxide composition obtained is intended for a catalyst to be used in reduction of NO with CO and oxidation of CO to CO_2 in gas mixtures.

For comparison Cu–Co oxide catalysts (KA_1–KA_3) and regenerated Pd catalyst with content of 2% Pd (catalyst KN) were used. It was established that not only the catalyst activity towards NO reduction with CO, but also the resistance to poisoning with SO_2 increased in the presence of Pd in combination with the synthesized fresh active Cu–Co phase.

In this way the 3KN catalyst is suitable to be used as a catalyst for purification of polluted gases.

Keywords: Pd catalyst; Oxide catalyst; CO oxidation; NO reduction

1. Introduction

Some spent supported catalysts contain valuable metals whose extraction would be desirable. Some contact masses have to be regenerated and reintroduced to industry. There are publications in literature [1–9] reporting some methods for regeneration of certain types of catalysts and extraction of platinum group and other valuable metals such as Ni, Co, Mo. Trivial technologies for metal extraction and catalyst regeneration require significant capital and energy investment, which reduces the effectiveness of the processes.

On the other hand, the deactivated catalysts are polydispersed systems and at the same time represent mixtures with different granulometries due to the different degrees of destruction of the catalyst granules during their exploitation. The question about utilization of the solid residue of supported catalysts after extraction of the useful components has not yet been answered. Although extraction methods have been improved there are still minimum concentrations of valuable metals (Pd, Pt < 0.1%) in the solid residue.

The purpose of the present paper is to check the possibility of using, after Pd extraction, the residue of deactivated Pd on alumina catalyst as a component of an oxide composite as well as to establish the effect of Pd on the catalyst activity. The polyoxide composition obtained is intended for a catalyst to be used in reduction of NO with CO and oxidation of CO to CO_2 in gas mixtures.

2. Experimental

The solid residue of a spent corundum-supported Pd catalyst for nitric acid production by high-temperature decomposition of NO_x in presence of a reducing agent was used for the experiments. The Pd content in this residue was 0.093% and the alumina Al_2O_3 was present as a corundum phase [1]. The oxide catalyst was obtained by addition of 10% bentonite as a plasticizer necessary for giving the composite the desired form, after which the granules were impregnated with a mixture of nitrate solutions of Cu–Co. The active phase has been deposited by a technology described in [10]. The Cu/Co ratio corresponded to the stoichiometry of the $CuCo_2O_4$ spinel. The catalyst was calcined at $T = 550\,^{\circ}C$ for 3 h (Catalyst 3KN). Contact oxide masses were synthesized in a similar way on a fresh catalyst with a precursor composition of bemite/bentonite calcined at

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doi:10.1016/j.cej.2006.03.016

Table 1
Contact mass characterization before impregnation

Support	Calcination temperature $T_{\text{calc.}}$ (°C)	Duration of calcinations (h)	Specific surface area (m^2/g)	Porosity θ (%)	Water absorbability (%)	Mechanical strength (kg/cm^2)
A_1	800	10	140	55	40	400
A_2	1000	6	85	48	35	450
A_3	1150	3	18	45	25	650
OB	1000	3	3	38	20	500

different temperatures for different times. The Al_2O_3/bentonite ratio in the calcined supports was 9:1. The Cu–Co active phase was identical with that of the 3KN catalyst. The method used for synthesizing fresh KA_1–KA_3 catalysts was dry mixing. The bemite phase precursor has been obtained by the method of continuous precipitation from the initial reagents (aqueous solution of aluminum nitrate and NH_4OH) followed by bentonite addition [11]. The solid residue composite has been mixed in a similar way with 10% bentonite containing 0.09% Pd (OB). After giving the contact masses the desired form, they were calcined at temperatures ranging from 800 to 1150 °C. Calcination after impregnation also proceeded at $T = 550$ °C in the course of 3 h (catalysts KA_1–KA_3). The phase composition of supports and catalysts was established by X-ray diffraction using a TUR (Germany) apparatus with Cu K(radiation. The specific surface area was measured by an express adsorption method and the total porosity was determined by impregnation of the samples with a low-molecular boiling liquid (benzene). Water absorption was determined during boiling in aqueous medium for 1 h. The mechanical strength of the tabletted supports was evaluated during their axial and radial destruction. The test was performed with a hydraulic press. The ICP analysis was made with a JY 39 spectroanalyser (France) in order to determine the Pd, Cu and Co concentrations in the samples. XPS analysis of some samples was performed using an ESCALAB Mk II VG Scientific apparatus with Al Kα line of 1486.6 eV. Calibration of the spectral lines was made on the C 1s line (285 eV).

The activity test of the catalysts with respect to NO reduction with CO was carried out on the flow apparatus. The samples granulometry was 0.3–0.6 mm. The investigation was carried out with carrier gas argon of purity 99.99%, with a volume rate $W = 26000\ h^{-1}$, and gas mixture NO + CO + Ar in stoichiometric. NO was about 1200 ppm, CO was 1200 ppm, thus RO = [CO]/[NO] = 1 ± 0.05 [12,13]. The same apparatus was used for temperature programmed desorption (TPD). The deviation of the temperature maxima of the TD peaks was ±5 °C. Nitrogen oxide and carbon monoxide were measured with UNOR (Maihak, Germany) gas analysers with accuracy <2%. Carbon monoxide was analysed at the reactor inlet with Infralyt 2106 (Germany). At the reactor outlet CO_2 was examined by an Infralyt 2106 (Germany) gas analyser again. The analysis of N_2O was made with a multiway gas cuvette from the firm Specac (England) mounted on Specord 75 IR (Germany). The results were interpreted by the transient response method, which is based on analysis of the type of response curves for the reaction products and permits determination of the rate controlling step of the reactions [14]. The catalytic oxidation of CO by oxygen from the air in the presence of catalytic poisons (SO_2) also took place in the flow apparatus described in [15]. The volume rate during the investigation was 20,000 h^{-1} at $T = 400$ °C in presence of the gas mixtures: CO (0.5 wt.%), O_2 (1 wt.%) and CO (0.5 wt.%), SO_2 (0.03 wt.%), O_2 (1 wt.%) and nitrogen as a carrier gas. The analysis of CO and CO_2 was performed with a Maihak, Germany, gas analyser, while the SO_2 content was controlled with Quintox (England).

Table 2
Composition and parameters of the catalysts

Sample	Composition (%)			Specific surface area S (m^2/g)	Porosity θ (%)	Mechanical strength (kg/cm^2)
	Cu	Co	Pd			
$2KA_1$	4.5	3	–	110	50	420
$2KA_2$	3.8	3.3	–	70	45	475
$2KA_3$	2.4	3.2	–	8	40	680
3KN	1.6	2.2	0.09	4	40	660
KN	–	–	2	2	30	400

3. Results and discussion

The XRD data show that various Al_2O_3 modifications are prevailing in the supports. The following phases have been observed:

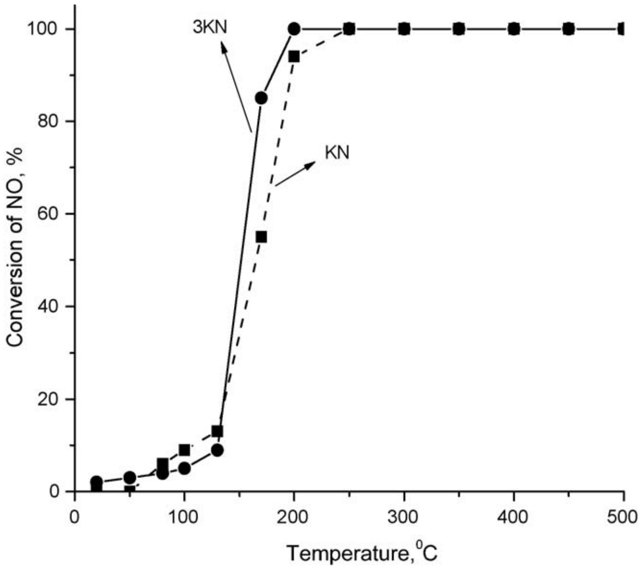

Fig. 1. Dependence of the degree of NO conversion on temperature for samples 3KN and KN.

In the supports:

- A_1—γ-Al_2O_3 (JSPDS PDF 10–425);
- A_2—$\gamma + \delta$-Al_2O_3 (JSPDS PDF 16–394);
- A_3—α-Al_2O_3 (JSPDS PDF 10–173).

The reflexes of silicon-containing phase are observed only in sample A_3 where there is a vague indication of the presence of mullite ($d = 3.42$ and 3.37). The appearance of mullite at these lower sintering temperatures is due to the method of precursor preparation which is carried in a homogeneous medium. The mullite formation temperatures in classical mullite ceramics are above 1150 °C [11]. With rising calcination temperature the crystallinity of alumina increases. The diffraction pattern of the residue of spent Pd catalyst (OB) shows the features of corundum (α-Al_2O_3—JSPDS PDF 10–173) only. All samples possess a high mechanical strength combined with the physicochemical parameters needed for deposition of the active Cu–Co phase. These qualities depend on the bemite precursor, which is dominant in the contact composition (Table 1). The porosity and water absorbability of support A remain high over the whole temperature range of 800–1150 °C. The OB contact mass has a small specific surface area as a result of the catalyst corundum structure and its prolonged exploitation under industrial conditions. The total porosity and water absorbability permit simultaneous deposition of the active oxide phase and investigation of the possibility of utilization of the spent catalyst as a component of fresh oxide catalyst.

After deposition of the active components, the specific surface area of the supported catalysts decreases. The other parameters undergo no drastic changes (Table 2). The mechanical strength increases, which is favorable for these catalysts as they work under conditions of local overheating and thermal shocks.

ICP analysis shows a difference in ratio of the active phase components although the impregnation method, initial solutions and granulometry of the oxide mass are the same. Here the difference in affinity towards the metal ions of the impregnating solution also plays a role. The phenomenon is ascribed to the so-called "chromatographic effect" of the support at 800–1000 °C. When a corundum or spinel-like modification (catalysts $2KA_3$

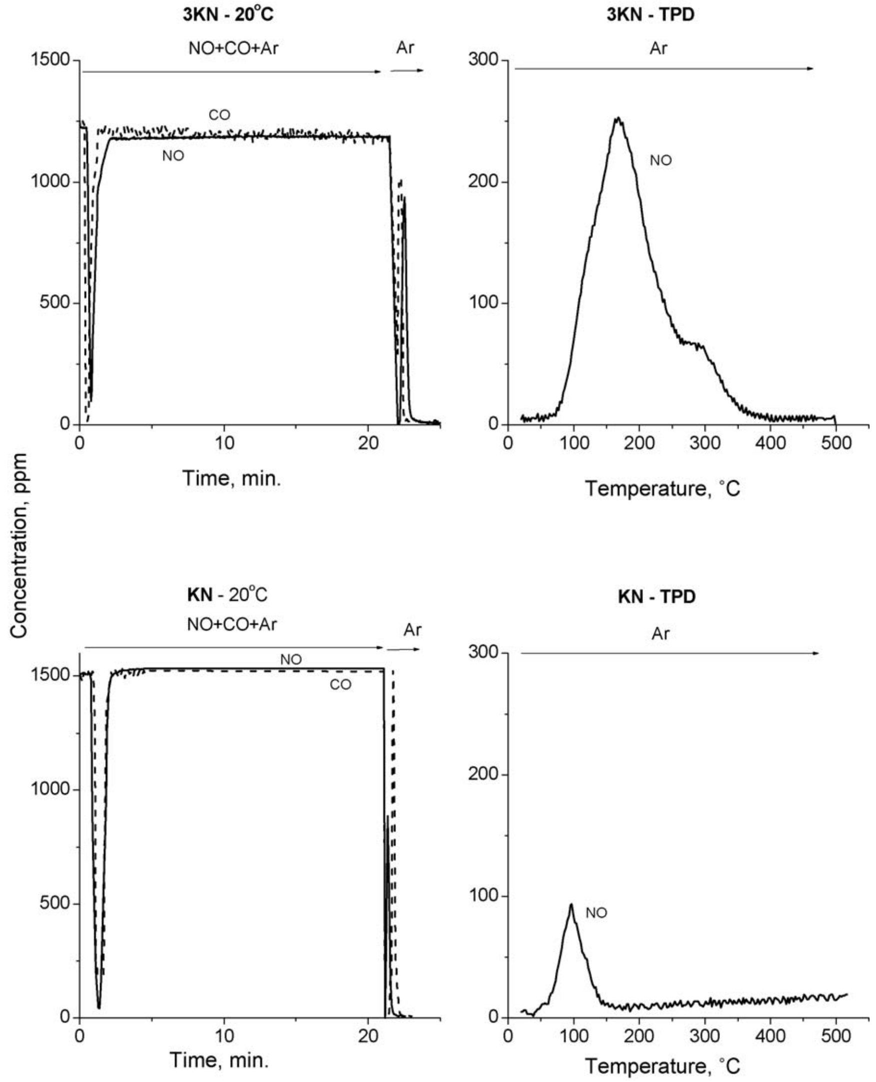

Fig. 2. TPD spectra of samples 3KN and KN.

and 3KN) is present in the support, this effect is absent. As a result, the catalysts obtained contain Cu in excess of the stoichiometric amount. [16,17]. Fig. 1 illustrates the dependence of the conversion of NO on temperature within the interval 25–500 °C, for the samples KN and 3KN. Both these samples show a high degree of NO reduction. At 170 °C the sample containing an active oxide phase (3KN) has a conversion degree of 85% while at the same temperature the Pd containing catalyst (KN) leads to an NO conversion of up to 55% (Fig. 1). This unambiguously shows the favorable effect of the active Cu–Co oxide phase regardless of the lower Pd content. Within the whole temperature range investigated the reaction proceeds to N_2, no N_2O being registered.

The results obtained by the transient response method for catalyst 3KN show that the regeneration of the catalytically active sites is rate determining. This confirms the opinion that with redox reactions such as NO reduction with CO, the activity is determined by the formation of active sites of metal ion pairs of transition elements in different oxidation states [18]. The TPD studies on catalyst KN show one desorption peak for NO at 100 °C while with catalyst 3KN, NO is desorbed at three temperatures: 100, 170 and 300 °C (see Fig. 2).

Probably, there is only one form of NO adsorption on the surface of the Pd containing catalyst. The presence of the three desorption peaks in the case of 3KN indicates the presence of three forms of NO adsorption, which is in accord with the results obtained from the response curves in concern of the presence of a new active phase. The results from TPD of the oxide catalyst KA_1 under the same conditions show an NO peak at 133 °C and a shoulder to the high-temperature part at 180 °C. The catalysts KA_2 and KA_3 do not differ with respect to peak maximal half-width and area ratio. Probably in the low-temperature region NO and CO react on the surface of the Cu–Co spinel according to a Langmuir–Hinshelwood mechanism. In the high-temperature region the mechanism of NO reduction changes from the mechanism of surface collision interactions into a mechanism of successive transformations, which is characteristic of a catalyst with oxide spinel phase. Under the effect of this active phase, a decrease in the lift-off temperature occurs. The difference between the activities of the Pd containing catalysts KN and 3KN is due to a dispersion change of the active component as a result of the exploitation of the Pd catalyst. In spite of the higher Pd content in catalyst KN, the expected higher activity is not observed. In the case of catalyst 3KN the Pd content is much lower but the deposition of a fresh oxide phase combined with some platinum group metal leads to the lowest starting temperature. The most favorable ratio between the active oxides phases in the oxide catalysts $2KA_1$ and $2KA_3$ (Table 3) is obtained when the support has been calcined above 800 °C, i.e. with catalysts $2KA_2$ and $2KA_3$. Table 3 shows that these two catalysts have the lowest starting temperatures with respect to both NO reductions with CO and CO oxidation to CO_2.

The above activities of catalysts KN and 3KN are also confirmed by the XP spectra. With the simultaneous deposition of Cu and Co, aimed at spinel formation, the Cu 2p lone was compared with that of $Cu_xCo_{3-x}O_4$ and CuO (see Fig. 3).

Table 3
Activity of the catalyst samples

T (°C)	Sample/activity (%)					
	$2KA_1$		$2KA_2$		$2KA_3$	
	CO	NO	CO	NO	CO	NO
100	–	–	–	3	–	3
150	–	3	3	15	45	27
200	67	7	82	25	82	45
250	80	38	95	55	95	58
300	80	38	95	55	95	60

A broad main peak at 934.3 eV showing a slight asymmetry to the low binding energies characterizes the Cu 2p spectrum of the catalyst 3KN. Comparison of the spectra of 3KN with standard of CuO and $Cu_xCo_{3-x}O_4$ shows that the main peak is similar to that of the oxide, whereas the satellite is similar to the satellite of the spinel. Comparing the Cu/Co ratio for catalyst 3KN with that for the stoichiometric spinel one can see that the Cu amount on the catalyst surface is about three times larger, as already established in [19]. The structural imperfection of the support determines the formation of the Cu–Co oxide phase [20]. The slight asymmetry of the Cu line on the side of the lower energies for the catalyst under consideration shows the absence of a well-defined spinel phase. This is probably due to the larger amount of Cu on the surface and the effect of the support on the formation of an ordered crystal structure.

As far as the stability of the catalysts towards poisoning with SO_2 is concerned, restoration of the oxide catalysts activity is

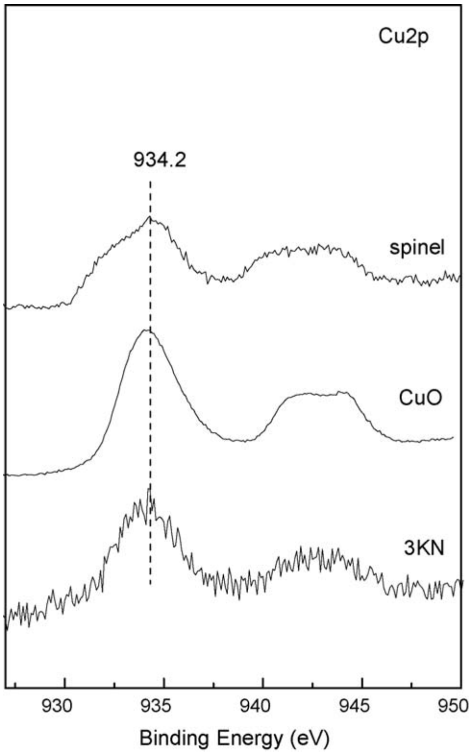

Fig. 3. Cu 2p photoelectron spectra of 3KN compared to the same of CuO and spinel.

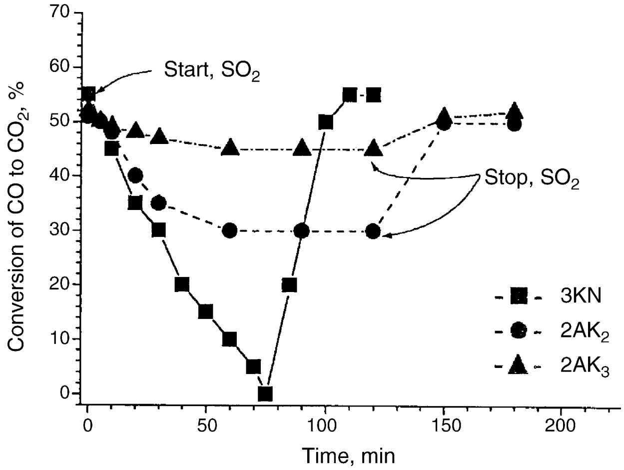

Fig. 4. The experimental results on poisoning of the catalysts 3KN, $2KA_2$ and $2KA_3$ by SO_2 during the reaction oxidation of $CO + O_2$.

observed, catalyst $2KA_3$ regaining completely its activity when the access of the poison is blocked (see Fig. 4).

The Pd containing KN sample is irreversibly poisoned. The stability of the oxide catalysts towards SO_2 can be attributed to the formation of aluminum phases in the composite support, capable to change the adsorption properties of the contact surfaces. This shows the role of the support with respect to the appearance of the most favorable surface-active phases. When SO_2 has no more access to the catalyst, its activity is restored.

4. Conclusion

The investigations performed are aimed to examine the possibility for using the residue of deactivated Pd/alumina catalyst, after extraction of Pd, as a component of an polyoxide composite. The obtained results show that:

- The presence of Pd in combination with the synthesized fresh active Cu–Co phase stipulates an increase of (i) the catalyst activity towards NO reduction with CO, and (ii) the resistance to poisoning with SO_2.
- An important role for the formation of a spinel-like active phase belongs to the structure and texture of the support precursors as well as to the solid-state processes occurring during the thermal treatment of the supports.
- The 3KN catalyst shows the highest activity and best restoration after poisoning. This gives grounds to assume that the residue from spent Pd containing catalyst may be applied as a component for fresh oxide catalysts. Thus, the technological cycle of treatment of the deactivated catalyst gets closed and the pollution from waste catalysts are diminished.

Acknowledgement

The investigations were performed with the financial support of the Ministry of Education and Science, contract no. 791.

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