

Complete Oxidation of Toluene on Co-Cr Mixed Oxide Catalyst

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Co-Cr mixed oxide system supported on γ -Al₂O₃ were studied by surface areas, thermoprogrammed reduction (TPR) and thermoprogrammed hydrogen desorption (TPHD) measurements. The catalytic activity of prepared catalysts were tested in the total oxidation of toluene at four concentration of toluene in air and at different temperatures and space velocities respectively. The catalyst prepared by successive impregnation exhibited higher activity than the catalyst prepared by precursor impregnation.

Keywords: toluene, oxidation, Co-Cr mixed oxides, supported oxide catalysts, tartaric acid complexes

Complete oxidation of hydrocarbons and of different organic compounds contained in waste gases is a well-developed procedure on platinum group catalysts [1-4]. However, searching for alternate, much more convenient and at the same time efficient oxide catalysts is at present the subject of many investigations. Total oxidation of toluene was a representative test for evaluating the performance of catalysts, particularly those related to the stability of the catalyst.

Perovskite oxides of LaMnO₃ were synthesized by sol-gel method in the presence of an oxide support, precipitating agent being citric acid [5]. The physico-chemical properties of the catalyst of LaMnO₃ were determined by N₂ adsorption-desorption, inductively coupled plasma atomic emission spectroscopy (ICP-AES), thermogravimetric and differential thermal analysis (TGA/DTA), X-ray diffraction (XRD), high transmission electron microscopy (HRTEM-EDX) and oxygen isotopic exchange analysis. The LaMnO₃ perovskite phase interacted with TiO₂ and Y₂O₃-ZrO₂ supports. This interaction influences the oxygen mobility and the catalytic activity for toluene oxidation. The catalytic stability was confirmed for all catalysts by long-term experiments. Supported materials showed a higher rate of oxygen exchange and a higher catalytic activity for the toluene oxidation than pure perovskite. This behavior of LaMnO₃/Y₂O₃-ZrO₂ could be attributed to the perovskite-support interaction and the oxygen vacancies of the Y₂O₃-ZrO₂. In the case of LaMnO₃/TiO₂ this behavior could be attributed to the activation of the support.

A support Au-Pd alloy catalyst in a molar ratio of Pd/Au 1.85/1.92 was used to prepare a catalyst on the basis of Mn₂O₃ using polyvinyl alcohol-protected reduction methods in the presence of a templating agent polymethylmethacrylate [6]. The catalytic activity of the catalysts was evaluated in the oxidation of toluene in a continuous flow fixed-bed quartz microreactor. Reactants and products were analyzed online by a gas-chromatograph (GC-2010, Shimadzu) equipped with flame ionization and thermal conductivity detectors, using a stabilwax-DA column for VOCs separation and a Carboxen 1000 column for permanent gas separation. All of the samples were characterized by means of techniques, such as ICP-AES, X-ray diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), etc. It appears that AuPd nanoparticles with a particle size of 2-4 nm were uniformly dispersed on the surface of Mn₂O₃ macroporous and the catalyst 3.8AuPd_{1.92}/Mn₂O₃ presented the best performance.

Moreover, even after the ignition has been very active 700[±]°C. The introduction of the water vapor in the raw material induces a positive effect for oxidation of toluene in this catalyst. Excellent catalytic activity, thermal stability, and water resistance of the catalyst 3.8AuPd_{1.92}/Mn₂O₃ macroporous was associated with better oxygen absorption on activated catalyst and strong interaction between noble metals and macroporous Mn₂O₃.

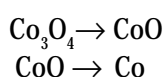
A series of mesoporous silica supported Pd catalysts with bimodal pore size were prepared by sol-gel method followed by impregnation technique [7]. The synthesized catalysts were characterized by XRD method, TEM micrographs, CO chemisorption using a dynamic pulse method and N₂ adsorption-desorption isotherms. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method and the pore volume and pore size distribution were estimated from the Barrett-Joyner-Halenda (BJH) model. Catalysts were used for the oxidation of toluene to evaluate their performance. Textural analysis showed that all samples had high surface areas (~1000 m²/g), large pore volumes (~1.2 cm³/g) and uniform mesopores size (~2.6 nm). Catalysts possess a typical bimodal mesoporous structure with an intraparticle framework mesopores and an interparticle textural mesopores (18-40 nm). Transmission electron microscopy observations and CO chemisorption results revealed that this unique bimodal mesoporous structure helped to decrease the particle size of Pd nanoparticles and could further enhance their dispersion. Activity tests revealed that the Pd/ bimodal mesoporous silica, prepared in the presence of smaller amounts of ammonia solution, possessed superior catalytic performance for the oxidation of toluene compared to the catalysts Pd/ mesoporous silica with a unimodal mesopore structure, prepared in the presence of higher amounts of ammonia solution. More importantly, compared with the Pd/MCM-41 and Pd/MCM-48 catalysts, Pd/bimodal mesoporous silica had improved hydrothermal stability and catalytic performance at a high gas hourly space velocity of 70000 h⁻¹. These results indicate the potential application of the catalysts for the elimination of volatile organic compounds.

Catalysts based non-noble metal are cheaper and may present high catalytic activity in the catalytic combustion of volatile aromatic hydrocarbons. Thus supported mixed oxides prepared from complexes of Co-Cr with tartaric acid may be used in complete oxidation of hydrocarbons. The active material of catalyst consist of mixtures of Co₃O₄ and CoCr₂O₄ obtained through the thermal decomposition of the double tartrate of cobalt and chromium.

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The XRD analysis of such resulted catalysts was carried out using a TUR-M62 device with HZG-3 diffractometer [8]. IR spectroscopy of such catalysts were obtained by means of a SPECORD 75 IR spectrofotometer, in the spectral range 4000 - 400 cm^{-1} . IR and electronic spectra as well as magnetic measurements have indicated that both COO^- and partially HO^- are coordinated at metallic ions in the precursors [8]. The main characteristic IR absorption bands of the catalysts are specific to functional groups present in the catalyst precursor. Thus, a large and intensive absorption band at 3400 - 3100 cm^{-1} and sharp and weak bands at 2920-2880 cm^{-1} , are typical for stretching vibrations of associated HO^- groups of tartaric acid and H_2O respectively (ν_{OH}) and could be found in all the samples. The bands at 1640 - 1580 cm^{-1} as well as the sharp band at 1375 cm^{-1} are usually attributed to asymmetric stretching vibration and symmetric vibration of the C-O bonds in carboxylic ion, respectively. These are also common to all samples and could be assigned to mixed Co-Cr tartaric acid salts. The bands at 1130-1000 cm^{-1} are attributed of the O-H bonds in carboxylic ion and the bands at 840-700 cm^{-1} are attributed of the C-C bonds in R radical. Sharp and weak bands are found in the region 680-510 cm^{-1} which are attributed to Me-O bonds. These are sometimes screened by intensive absorption bands of the supports. Finally, partial coordination of the organic ligand takes place even, via both COO^- and HO^- groups.

The transformations of the complexes into oxides were checked by TGA analysis. The thermal analysis of the such catalysts was carried out using a DuPont 1090 Thermal Analyzer with 951 TGA module, within the temperature range of 20-500°C. Although the weight loss processes end at 550°C for all samples, the tested catalysts were calcined at 650°C, in order to stabilize the oxide phase. XRD spectra of the calcined samples revealed a solid solutions of Co_3O_4 , CoCr_2O_4 on the copper-chromium supported catalysts [9]. The X-ray diffraction data of the such unsupported catalyst showed the existence of a solid solution of Co_3O_4 and CoCr_2O_4 . In the samples supported on $\gamma\text{-Al}_2\text{O}_3$, only the crystalline forms of the supports, were identified. The TPR of Co_3O_4 with hydrogen showed two peaks [10-13] located at 320 and 390°C assigned to the transformations:



The presence of the support as well as the introduction of Cr^{3+} ion in the spinel structure of Co_3O_4 decreases its reducibility [14,15].

In this paper is studied the synthesis of Co-Cr mixed oxide catalysts from complexes of Co-Cr with tartaric acid. These materials were deposition by impregnation on $\gamma\text{-Al}_2\text{O}_3$ tablets. The catalysts were tested in the complete oxidation of toluene, at 700, 1000, 1500 and 2000 p.p.m. concentration of hydrocarbon in air and at 5000- 20000 h^{-1} space velocity.

Experimental part

The raw materials used in experiments were cobalt(II) nitrate hexahydrate and chromium(III) nitrate nonahydrate puriss p.a. (Sigma-Aldrich), nickel(II) nitrate hexahydrate puriss p.a. (Sigma Aldrich), tartaric acid ACS reagent, $\geq 99.5\%$ (Sigma-Aldrich), γ -alumina tablets ($\phi = 6$ mm), toluene anhydrous, 99.8% (Sigma-Aldrich) and ammonium hydroxide solution, ACS reagent, 28.0-30.0% NH_3 basis (Sigma-Aldrich).

The precursor complexes were obtained by precipitation at pH 7 of aqueous solution Co-Cr nitrates and tartaric acid, mixed with a 1:1 solution of ethanol and ammonium

hydroxide 10%. After precipitation, the resulted compound was dried in vacuum at 90°C.

In order to prepare the supported catalysts two procedures have been used:

- the first one consists in the synthesis and binding of the precursor on the support by successive impregnation of the solution of tartaric acid and of the nitrate mixtures;
- the second procedure consists in solubilization of the pre-prepared precursor and its deposition on the support by impregnation on γ -alumina support tablets.

The metal weight content of the resulted samples was 8.5% - 10%. Supported catalysts have been dried for 12h at 90°C and calcined at 650°C for 6h. The following notations of the prepared catalysts are used: C_3 catalyst prepared by the first procedure (successive impregnation), whereas C_7 catalyst by the second one (precursor impregnation).

The surface areas, TPR and TPD measurements were performed on CHEMBET -3000 apparatus. A linear heating program was applied, with a rate of 10 K min^{-1} and within the temperature range 20 - 500°C. Catalyst samples of 0.11 g were introduced in the stainless steel reactor and pretreated in flowing argon at 500°C for 4 h. After cooling in flowing argon to room temperature, the carrier gas was switched to the mixture $\text{Ar}+3\% \text{H}_2$ and the baseline was stabilized; the system was then heated to 500°C with 10 Kmin^{-1} , while the hydrogen consumption from the carrier gas yielded the first heating cycle record (HCR1). The sample was kept at 500°C until the baseline was stable and then cooled in argon to room temperature. After switching to the gas mixture and baseline stabilization, the heating program was again applied and the second heating cycle record (HCR2) was obtained. The sample was then cooled at room temperature in the flowing gas mixture in order to saturate it with hydrogen, after which the carrier gas was switched to argon. After stabilizing the signal, the sample was linearly heated to 500°C and the TPD curve was recorded.

The catalytic activity of the samples was measured in a flow reactor using a mixing system, a thermostat regulator for hydrocarbon vapor control and air flow controls. The analysis was carried out with an in line Hewlet Packard Gas Chromatograph model 5840A provided with Chromosorb 102 and Porapak Q packed columns.

The catalysts were tested in the complete oxidation of toluene, at 700, 1000, 1500 and 2000 p.p.m. concentration of hydrocarbon in air and at 5000- 20000 h^{-1} space velocity.

Results and discussions

The surface areas of the investigated samples are presented in table 1. The slightly lower surface areas of uncalcined samples is ascribed to the partial blocking of the porous structure of the support, with either complex precursor or its individual components (successively deposited).

Figures 1 and 2 show the TPR results for supported catalysts C_3 catalyst and C_7 catalyst. As one can see from these figures, the different preparation procedures result in differences in the hydrogen consumption which is twice higher for the sample C_3 catalyst in HCR1. For HCR1 both samples exhibit a peak at approximately 400°C, but to a lower extent.

The TPD curve for sample C_3 catalyst and C_7 catalyst is given in figures 3 and 4. The both samples give similar TPD curves characterized by continuous increase in hydrogen presence at temperatures higher than 300°C.

Depending on the experimental conditions, as well as on the investigated temperature range, as many as four TPR peaks located between 400 and 800°C have been

Sample	γ -Al ₂ O ₃	C ₃ catalyst	C ₇ catalyst
Uncalcined samples, m ² /g	-	143	126
Calcined samples, m ² /g	161	175	140

Table 1
THE SURFACE AREA OF THE SAMPLES

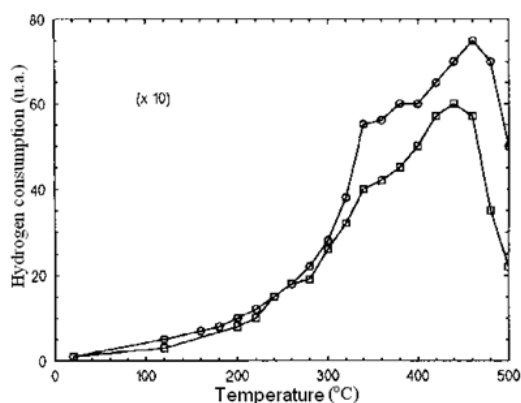


Fig.1 HCR1(O) and HCR2 () for C₃ catalyst

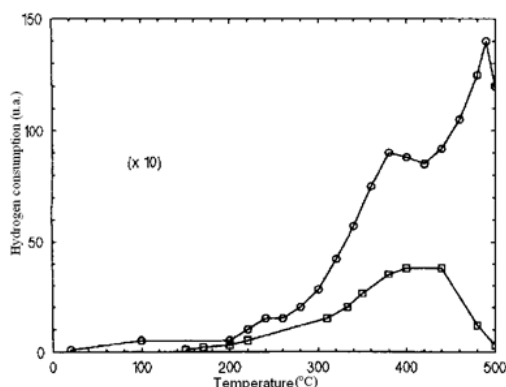


Fig.2. HCR1 (O) and HCR2 () for C₇ catalyst

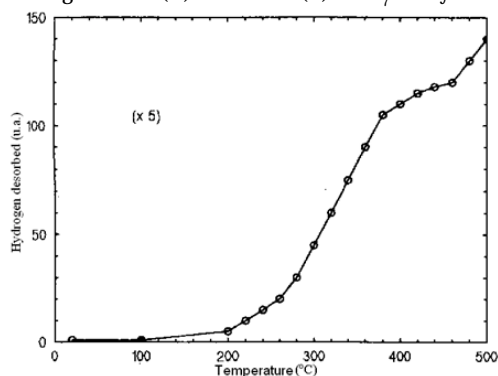


Fig.3 TPD curve for C3 catalyst

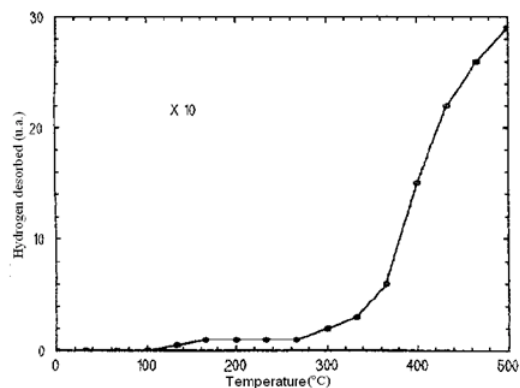


Fig.4. TPD curve for C7 catalyst

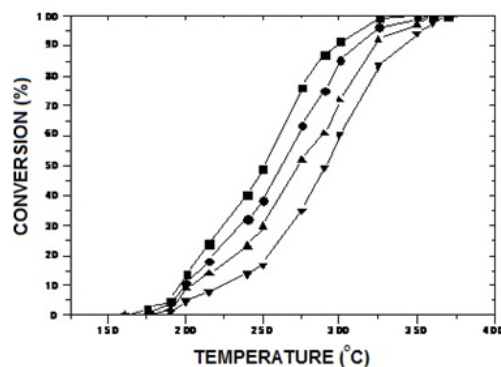


Fig.5 Variation of conversion with temperature at 700 ppm (■), 1000 ppm (●), 1500 ppm (▼), 2000 ppm (▲) concentration of toluene in air and 20000 h⁻¹ space velocity on C₃ catalyst

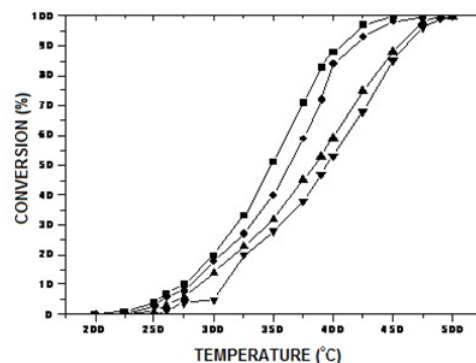


Fig.6. Variation of conversion with temperature at 700 ppm (■), 1000 ppm (●), 1500 ppm (▼), 2000 ppm (▲) concentration of toluene in air and 20000 h⁻¹ space velocity on C₇ catalyst

found for Co₃O₄ [16]. Total reduction to metallic cobalt may occur after keeping the sample for a long time at 500°C.

The results obtained using the TPR method confirm those obtained by X-ray diffraction, as well as the results of the authors [14-16]. The existence of HCR1 and HCR2 show that the first heating cycle of the sample with hydrogen does not determine the total reduction. The reduction is activated and it occurs in a certain time. Moreover, the sharp peak from HCR2 at 280°C may be interpreted as oxide which lead to a surface reconstruction. As expected, the supported samples give wide peaks due to the higher surface non-uniformity. The existence of HCR2 is probably due to the adsorption of hydrogen on the metallic clusters that appeared during reduction to cobalt as well as to reduction of the oxide traces.

The results obtained by TPD measurements show that hydrogen is strongly bound to the surface and can be desorbed only at temperatures higher than 300°C. No weakly bound hydrogen was detected by the applied methods. The existence of strongly adsorbed hydrogen which can be desorbed at high temperatures was confirmed by our TPD experiments.

The catalytic activity of the prepared catalysts, in the total oxidation of toluene, is illustrated in Figs. 5 and 6 in the form of conversion - temperature plots, obtained at 700, 1000, 1500 and 2000 p.p.m. concentration of toluene in air and space velocity 20000 h⁻¹.

The C₃ catalyst are highly active in the complete oxidation of toluene, even at temperatures below 350°C. The C₇ catalyst are a similar activity at temperatures with 100°C more highly.

Conclusions

The presence of the support lowers the reductibility of the sample, thus indicating a strong interaction with oxides.

Below 500°C, the reducible forms are Co_3O_4 and CoO . At higher temperatures the desorption occurs for hydrogen adsorbed on the metallic forms which appeared on the surface due to the reduction.

The active phase of this catalyst is the solid solution of Co_3O_4 and CoCr_2O_4 .

Better activity and stability of the cobalt-chromium catalysts in the complete oxidation of aromatic hydrocarbons was evidenced.

With respect to the method of preparation, the catalysts obtained by precursor-complex formation directly on the support are more active (C_3 catalyst).

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