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SIZE-DEPENDENT EFECTS

Particle size and support effects on the complete benzene oxidation by Co and Co–Pt catalysts

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Abstract Monometallic cobalt and bimetallic Co–Pt samples of various particle sizes have been prepared using SiO_2 and synthetic kenyaite (layered silicate) as a support. They are characterized by elemental analysis, XRD, TPR, and XPS. Cobalt is introduced by two methods—classical impregnation and ammonia method. The ammonia method of preparation leads to the formation of finely dispersed Co_3O_4 on both supports. Besides, hardly reducible cobalt silicate phases appear predominantly on the SiO_2 support. The Co_3O_4 particle size varies between 5 and 20 nm, depending on the support. The monometallic Co samples prepared by ammonia method on both supports are more active in benzene combustion than the impregnated ones due to the finer dispersion of the easily reducible Co_3O_4. Addition of Pt improves the activity and the promoting effect is more evident for the impregnated sample. This is explained with the synergy effect of cobalt oxide species and Pt. The less promoting effect of Pt on the catalytic activity of the bimetallic kenyaite-supported samples is attributed to the stronger interaction between the Co oxide phase and Pt during the preparation process.

Introduction

The design of a catalytic system for complete oxidation of hydrocarbons is an important problem of the environmental catalysis. Volatile organic compounds (VOC) are the major contributors to air pollution. Catalytic oxidation is one of the most important processes for VOC elimination, since the catalytic incineration takes place at temperatures much lower than those required for thermal incineration. It is well known that the complete VOC oxidation catalysts can be classified into three categories: (1) supported noble metals; (2) metal oxides or supported metal oxides; (3) mixtures of noble metal and metal oxides. Major part of the commercial catalysts for VOC destruction belongs to the first category, because the reaction can start at temperature as low as room, but their cost is high. Transition metal oxides are less efficient, but more resistant at high temperatures.

Cobalt oxide is reported to be quite promising among the metal oxides used for preparation of supported catalysts for the removal of CO [1, 2] and VOC [3–7]. There are investigations according to which good cobalt catalysts for methane combustion [5] and propane oxidation [6] are those of high cobalt dispersion. The active phase dispersion in supported catalysts is known to control their activity. The following factors influence the active phase dispersion: support type, method of preparation, calcination conditions, precursors and active phase loading. Even though cheaper, cobalt taken alone is not so active in reactions of complete VOC oxidation and the addition of Pt may enhance the catalytic activity by increasing the reducibility of Co oxide. Oxidation of hydrocarbon by oxygen proceeds by partial reduction of the oxide and the rate-determining step of the reaction is

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the reoxidation of the reduced solid. Addition of a small amount of platinum catalyses that reoxidation [8].

The aim of the present work is to establish the influence of the cobalt oxide dispersion and the support type on the catalytic activity in the reaction of complete benzene oxidation. Silica and synthetic kenyaite have been used as supports for the preparation of monometallic cobalt and bimetallic Co–Pt catalysts.

Experimental

Sample preparation

SiO_2 (Aerosil A, S = 380 m^2/g) and synthetic kenyaite (S = 150 m^2/g) were used as carriers for sample preparation. Kenyaite (named in the text Ken) was prepared according a procedure described in Ref. [9].

Cobalt was loaded on the supports by two methods. Classical impregnation with aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ was used to prepare the precursor which was subsequently dried and calcined for 1 h at 773 K in air (samples designated from here on as samples I). The second method applied is described by Barbier et al. [10] as ammonia method. It leads to the formation of finely dispersed cobalt oxide on the support. In a typical procedure $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in water at room temperature. To prevent oxidation of Co^{2+} by dissolved oxygen the water was boiled and the system was protected from air by a nitrogen blanket. After that ammonia was added to the solution. The role of ammonia is 3-fold: (1) Functionalization of the silica surface: $Si–OH + NH_3 = SiO–NH^{4+}$; (2) Formation of cobalt amine ions $[Co(H_2O)_{6–n}(NH_3)_n]^{2+}$, which are exchanged with surface NH^{4+} ions; (3) Precipitation of part of cobalt as $Co(OH)_2$.

The support was added to the solution and stirred for 2 h. Finally, the system was filtered, washed with distilled water, dried under vacuum at 353 K and calcined for 1 h at 773 K in air (samples designated from here on as samples AM).

Platinum was introduced by impregnation with aqueous solution of $Pt(NH_3)_4Cl_2$ on the Co-containing supports after their calcination except for the kenyaite sample (Co/Ken-AM) where impregnation was performed on the freshly prepared (not calcined) precursor. Platinum-loaded samples were dried overnight at 373 K and calcined additionally for 1 h at 773 K in air. Monometallic platinum samples were prepared by impregnation on both supports in order to compare their catalytic activity with that one of the other samples.

Sample characterization

The powder XRD patterns were collected at room temperature in a step-scan regime (step = 0.02°, count time = 2 s) on a DRON 3 M diffractometer using Fe-filtered CoKα radiation (λ = 1.7903 Å). The XRD data were processed using the programme FIT [11].

Temperature programmed reduction (TPR) was carried out in equipment described elsewhere [12], using a flow mixture 10% H_2 in Ar at 10 ml/min, temperature ramp of 10 K/min to 973 K. Prior to the TPR experiment the samples were treated in Ar for 1 h at 423 K. XPS spectra were recorded on ESCALAB-MkII (VG Scientific) electron spectrometer with base pressure 1×10^{-8} Pa, following the technique given in Ref. [13]. The energy position of the photoelectron lines was determined with respect to the reference C1s line (Binding Energy—BE, 285 eV). Specific surface area measurements for the calcined samples were carried out on Micromeritics instrument FlowSorb 230, using single point surface analysis. The amount of Co and Pt in the catalysts was determined by Varian ICP AES.

Catalytic test

The samples were tested in the reaction of complete benzene oxidation. The tests were carried out in a flow type glass reactor at atmospheric pressure. The catalyst loading was about 100 mg, fraction 0.8–0.63 mm. The external mass transfer limitations were minimized by working at high GHSV (37,500 h^{-1}). Also the reactor diameter is 8 mm i.d. so the ratio of Dr/Dp = 11 ensures weak effect of the radial gradient. The catalyst temperature measurements were performed by a thermocouple positioned in the catalysts bed. The inlet benzene concentration was about 1,400 ppmv at a total flow rate of 250 ml/min. The reaction products were analysed by a Varian 3700 gas chromatograph equipped with thermal conductivity detector (T = 333 K, $T_{filament}$ = 353 K), flame ionization detector (T = 453 K) and 2 m column with Porapak Q (0.150–0.180 mm, Riedel-de Haën AG D-3016 Seelze 1) operating at 443 K. Nitrogen was used as a carrier gas (30 ml/min). All gas lines were heated at 353 K in order to minimize the VOC adsorption on the tube walls. Mass flow controllers Matheson were used for stable control of the gas flow rates. Benzene (Merck) was used both for oxidation and calibration. The gas chromatograph was calibrated against known concentrations of benzene and the decrease in the peak areas was used as a measure of the conversion. The conversion was calculated as the quantity of benzene converted over that one of the introduced reagent.

Results and discussion

Sample characterization

Table 1 presents the metal content according to the elemental analysis, the surface area after metal deposition and Co_3O_4 particle size calculated according to Scherrer equation (see section "Sample characterization"). The XRD patterns of the monometallic (cobalt) samples after calcination are shown in Fig. 1. The reflections labelled with asterisks are characteristic for Co_3O_4. The samples prepared by ammonia method indicate average particle size of the metal oxide of about 9 nm for Co/SiO_2-AM and 5 nm for Co/Ken-AM. Particle size of 13 and 20 nm was registered in the samples prepared by impregnation on SiO_2 and kenyaite, respectively. Comparing the methods of preparation it is seen that the deposition of cobalt by impregnation both on SiO_2 and on kenyaite leads to the formation of relatively large Co_3O_4 particles (Table 1).

The TPR profile of Co/SiO_2-AM (Fig. 2a) manifests a shoulder at around 477 K and reduction peaks at 582, 643, 684 K and above 973 K. It is well known that the reduction of Co_3O_4 takes place in two steps—reduction of Co_3O_4 to CoO in the temperature interval 500–600 K and that of CoO to Co^0 in the interval 600–700 K [14]. Taking this into account the peak at 582 K is attributed to the reduction of Co_3O_4 to CoO and those at 643 and 684 K to the reduction of CoO to Co^0. The shoulder at 477 K could be associated with the reduction of O_2 chemisorbed on Co^{2+} ions [15]. The occurrence of several reduction peaks in the temperature interval of CoO reduction indicates the presence of a number of cobalt species in the catalysts.

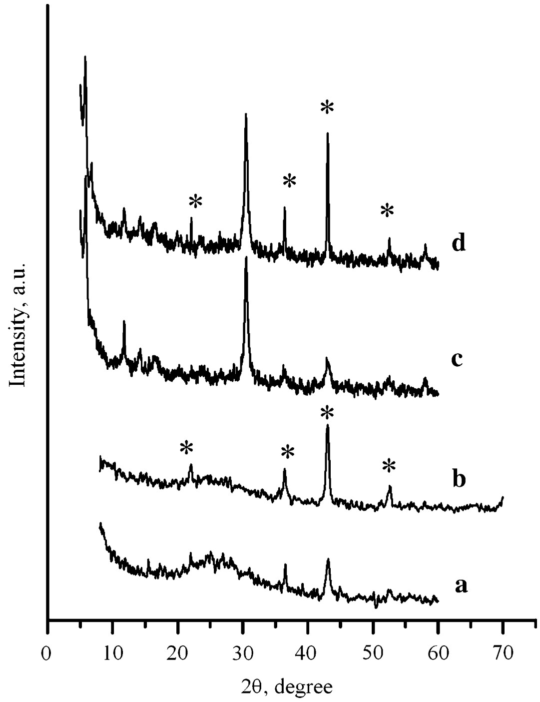

Fig. 1 XRD patterns of samples calcined at 773 K: (a) Co/SiO_2-AM; (b) Co/SiO_2-I; (c) Co/Ken-AM; (d) Co/Ken-I

Hydrogen consumption above 973 K is most probably a result of the supported cobalt silicate phase reduction. There are a large number of researchers according to which the cobalt containing phases on Co/SiO_2 that are reducible at temperatures above 973 K are those of silicates or hydrosilicates [16–19]. We suppose that, after calcination of the samples prepared by ammonia method, cobalt is mostly presented in the form of surface silicates. Addition of Pt to the calcined Co/SiO_2-AM promotes the reduction of all cobalt

Table 1 Sample characterization

Sample	Metal content[a]		Surface (m^2/g)	Mean particle size of Co_3O_4 (nm)[b]
	Co (wt%)	Pt (wt%)		
Co/SiO_2-AM	7.16			9
Co + Pt/SiO_2-AM	7.16	0.1	285	
Co/SiO_2-I	7.06			13
Co + Pt/SiO_2-I	7.06	0.17		
Pt/SiO_2-I		0.1		
Co/Ken-AM	7.59			5
Co + Pt/Ken-AM	7.59	0.06	140	
Co/Ken-I	11.77			20
Co + Pt/Ken-I	11.77	0.12	110	
Pt/Ken-I		0.06		

[a] According to the elemental analysis

[b] Calculated from XRD data

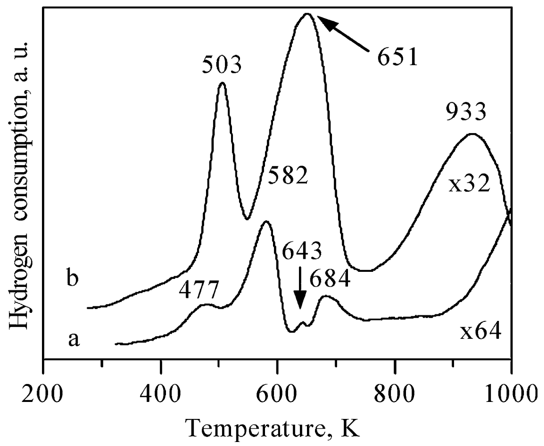

Fig. 2 TPR profiles of: (a) Co/SiO_2-AM; (b) Co + Pt/SiO_2-AM

oxide phases—the peak at 582 K shifts to lower temperature with about 80 K and the peak above 973 K splits in two with maxima at 651 and 933 K (Fig. 2b). The latter two peaks come very likely from reduction of cobalt silicate phase placed on the support whose reduction is promoted in a different manner by Pt.

The monometallic Co/SiO_2-I (Fig. 3a) exhibits two reduction peaks—the first one with a maximum at around 604 K and the second one with a maximum at 628 K. These two peaks fit well in the reduction interval of bulk Co_3O_4 powder or supported relatively large Co_3O_4 particles [14]. The TPR profile of the bimetallic sample is clearly different from that of the monometallic one (Fig. 3b). Two overlapping peaks at 415 and 448 K, a broad peak at 556 K and a small one at 664 K can be seen on the TPR profile. The presence of several reduction peaks after Pt deposition most probably is result of the presence of cobalt oxide particles located on different distances from platinum thus the promoting effect of the latter on the reduction is more or less pronounced.

The reduction behaviour of the kenyaite-supported cobalt samples was discussed in Ref. [9]. It was found that the ammonia method of sample preparation on kenyaite support promoted the formation of more dispersed Co_3O_4 particles as compared to the impregnation one (reduction peaks at 594 and 658 K for Co/Ken-AM, 654 and 667 K for Co/Ken-I).

The peaks for Co/SiO_2-I (Fig. 3a) appear at lower temperatures in comparison with those for the sample with kenyaite support. This is in accordance with the particle size effect—the smaller the particle size, the lower is the registered reduction temperature.

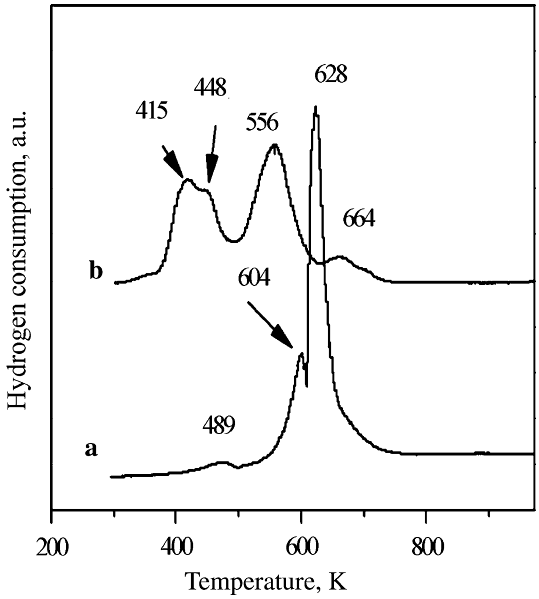

Fig. 3 TPR profiles of: (a) Co/SiO_2-I; (b) Co + Pt/SiO_2-I

Addition of Pt promotes the reduction of Co_3O_4 in all samples and the process depends on the noble metal content. It should be noted that a separate peak corresponding to the reduction of Pt oxide only was not observed in our experiments. This is due to the low Pt content and the high Co/Pt ratio in our catalysts leading to very small hydrogen consumption by platinum compared to that one for the reduction of cobalt oxide.

XPS spectrum of the Co + Pt/SiO_2-AM sample in the Co 2p region is shown in Fig. 4. The presence of Co^{2+} is confirmed by the Co $2p_{3/2}$ peak at 782.1 eV, accompanied by a relatively intense 3d → 4s shake-up satellite peak at 787.5 eV [20, 21]. Spin-orbital splitting upon ionization between $2p_{3/2}$ and $2p_{1/2}$, that is ca. 16 eV [21], is also observed. For the Co + Pt/SiO_2-I sample, the Co $2p_{3/2}$ peak is shifted to lower binding energy and the satellite peak, registered as a shoulder, decreases in intensity. The decrease in the shake-up contribution suggests formation of Co_3O_4, which is in accordance with the TPR and XRD data. The shift to lower BE results, probably, from the increase in the valence state of Co. The low intensity of the Co $2p_{3/2}$ peak (Fig. 5) for the impregnated catalyst is likely due to the formation of large CoO_x particles and thus lower cobalt surface concentration is detectable by XPS, respectively. There are not detectible peaks for bimetallic Co–Pt samples in the region of Pt $4f_{7/2}$ very likely because of low platinum concentration on the support.

Based on the results given above a conclusion could be drawn that the ammonia method of preparation leads to the formation of finely dispersed metal oxide particles. Depending on the support one or several

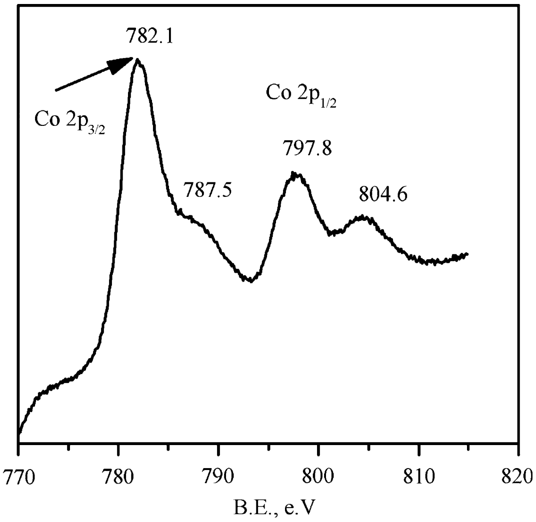

Fig. 4 Co 2p XPS spectra of Co + Pt/SiO_2-AM sample

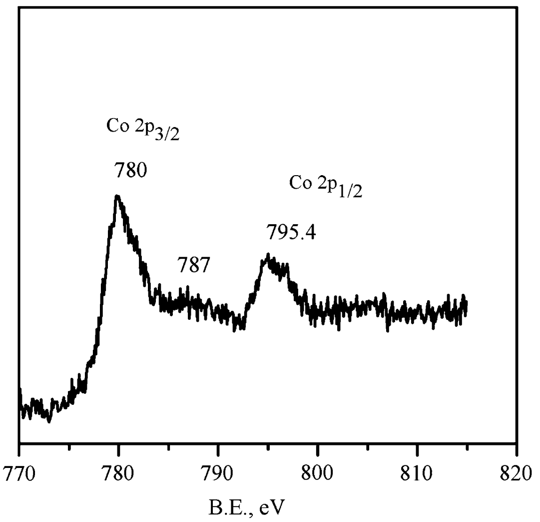

Fig. 5 Co 2p XPS spectra of Co + Pt/SiO_2-I sample

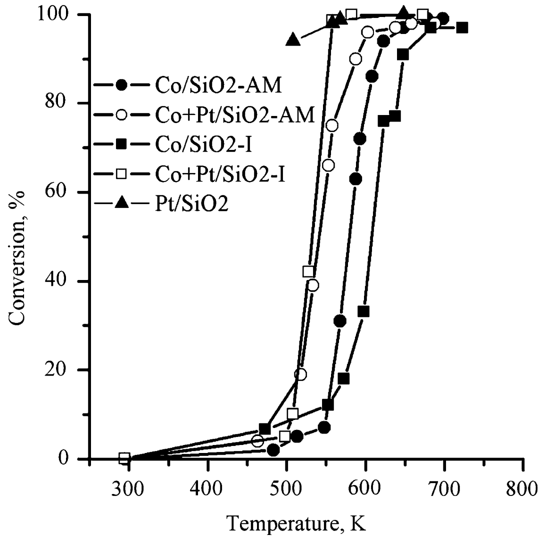

Fig. 6 Dependence of the conversion with temperature on the silica-supported Co and Co–Pt samples in the reaction of complete benzene oxidation

cobalt phases are formed. When SiO_2 is used as support, Co_3O_4, CoO phases located in different position on the support and cobalt silicate phases are formed. On the layered silicate kenyaite only finely dispersed Co_3O_4 is presented. Introduction of cobalt on both supports by impregnation leads to the formation of Co_3O_4 only.

Catalytic activity

The temperature dependences of the complete benzene oxidation over silica-supported catalysts prepared by both methods are shown in Fig. 6. H_2O and CO_2 were the only detectable reaction products.

The samples were compared according to the temperature for 50% (T_{50}) and 95% (T_{95}) hydrocarbon conversion or according to that one for maximum conversion in cases when the value of 95% had not been reached. The activity of all prepared samples is presented on Table 2.

As can be seen from Table 2 and Fig. 6, the monometallic samples prepared by ammonia method are more active than impregnated one. It is well known that the transient metal oxides operate in complete hydrocarbon oxidation by redox type mechanism, according to which the oxide species oxidize the hydrocarbon and are regenerated by the oxygen-containing gaseous phase. In this way the catalytic behaviour can be correlated with oxide reducibility. The better performance in the reaction of complete benzene oxidation of the samples prepared by ammonia method on SiO_2 than that of catalysts on kenyaite, in spite of the lower dispersion of Co_3O_4 calculated from XRD data (Table 1), is due to the presence of a part of cobalt that is easier reducible as it is found with TPR (the peaks at T < 600 K in Fig. 2 and the lack of such peaks with Co/Ken-AM [9]). The higher surface area of silica than that of kenyaite (see Experimental) could also be important. Cobalt loading by impregnation leads to the formation of large Co_3O_4 crystallites (13 nm, see Table 1), which are reduced at higher temperature. Higher temperatures of cobalt reduction were registered with TPR of Co/Ken-I [9]. The higher activity at T_{95} for the Co/SiO_2-I (733 K) in comparison with the activity of Co/Ken-I (723 K, 76%) (Table 2) can be related to the lower particle size of Co_3O_4 in the former sample and as consequence easy reduction of the cobalt oxide.

Addition of Pt to the cobalt catalysts improves their activity in the reaction of complete benzene oxidation.

Table 2 Catalytic activity data presented as temperature at 50 and 95% conversion of benzene (T_{50} and T_{95})

	T_{50} (K)	T_{95} (K)
Samples supported on SiO_2		
Co/SiO_2-AM	580	640
Co + Pt/SiO_2-AM	540	603
Co/SiO_2-I	608	668
Co + Pt/SiO_2-I	530	560
Pt/SiO_2-I		526
Samples supported on kenyaite [9]		
Co/Ken-AM	580	700
Co + Pt/Ken-AM	570	640
Co/Ken-I	653	723 (76% conversion)
Co + Pt/Ken-I	525	705 (90% conversion)
Pt/Ken-I	521	640

The values in brackets show the maximum conversion reached in the studied temperature interval 298–723 K

This result can be explained by synergy effect of cobalt oxide species and Pt. In general, activity of the bimetallic supported samples is found to be lower than that one of Pt/SiO_2. One of the possible explanations is that Pt particles in the bimetallic samples are decorated by (or interact strongly with) cobalt during the pre-treatment as it has already been reported [22, 23]. Moreno-Tost et al. [22] have observed that at low concentration, Pt interacts strongly with the surface of the support or the cobalt phase and, as a consequence, its reduction has been impeded. Zsoldos et al. [23] have observed reduced concentration of Pt on the support when Pt and Co have simultaneously been deposited. The explanation given is that cobalt species have covered partially the platinum.

As can be seen from Table 2 and Fig. 6, platinum promotes in lower extent the ammonia prepared samples. One of the possible explanations can be a strong interaction between Pt and finely dispersed Co_3O_4 in these samples. The less promoting effect of Pt on the catalytic activity of bimetallic Co + Pt/Ken-AM in the reaction of deep benzene oxidation can be attributed also to the lower Pt concentration in this sample and to the strong interaction between Co oxide and Pt during the preparation process. As it is mentioned in section ‘‘Sample preparation’’, Pt has been introduced to the fresh (not calcined) sample of Co deposited by ammonia method on kenyaite. Very likely, the subsequent calcination has led to a strong interaction between Co_3O_4 and Pt, to decreased reducibility and accessibility of platinum and thus to a weaker promoting effect.

Conclusions

Supported monometallic (Co) and bimetallic (Co–Pt) catalysts with different particle size are prepared by impregnation and ammonia method. SiO_2 and synthetic kenyaite are used as supports.

XRD patterns and TPR profiles show that the ammonia method of preparation leads to the formation of finely dispersed Co_3O_4 on both supports. Difficult for reduction cobalt silicate supported phases, besides Co_3O_4, are formed mostly on the SiO_2. The better performance in the reaction of complete benzene oxidation of the samples prepared by ammonia method is due to finely dispersed and easily reducible Co_3O_4. Samples supported on SiO_2 exhibit higher catalytic activity than that on kenyaite, probably due to the presence of easier reducible cobalt. The higher surface area of silica than that of kenyaite could also be important. Addition of Pt improves the combustion activity and the promoting effect is more evident for the samples prepared by impregnation. This result can be explained by synergy effect of cobalt oxide species and Pt. The less promoting effect of Pt on the catalytic activity of bimetallic catalyst prepared by ammonia method on kenyaite support can be attributed to a strong interaction between Co oxide phase and Pt resulting from the procedure of catalyst preparation.

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