

Supported bimetallic Pd–Co catalysts: characterization and catalytic activity

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Available online 6 November 2004

Abstract

The aim of this contribution is to present a general overview about the effect of palladium addition to supported cobalt catalysts. First, the promotion of supported monometallic catalysts by the addition of a second component is described from a general point of view. Then, the properties of bimetallic Pd–Co supported on inorganic oxides are illustrated from the most relevant reports given in the literature. These works have been mainly performed on metallic catalysts under reducible atmospheres for important reactions like hydrogenation of butadiene, Fisher–Tropsch and methane activation under nonoxidative conditions. The last part is concentrated on Pd–Co zeolite-supported catalysts which have exhibited much more resistance to water vapor for lean NO_x reduction by CH₄ than either Pd or Co monometallic loaded zeolites under net oxidizing conditions. Recent results about the synergism of cobalt and palladium in zeolites and sulfated zirconia are discussed in terms of the effects of catalyst preparation and pretreatment, type of support and gas phase composition on the selectivity and stability of these catalysts for the selective catalytic reduction (SCR) of NO by methane.

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Keywords: Bimetallic; Co–Pd; Inorganic supports; Hydrogenations; Zeolites; Mordenite; Sulfated zirconia; NO_x reduction; Methane

1. Introduction

Supported bimetallic catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties of the other metal as a result of both electronic and structural effects. The promotion of the catalytic properties of one metal by addition of a second component, can be rationalized in the general frame of the “structure–activity” relationships, and has often been explained in terms of electronic and/or geometric effects [1]. Knowledge of the structural (ensemble) and electronic (ligand) effects is essential to catalyst optimization as both segregation and different adsorption properties may be explained by them [2]. Characterization techniques such as XRD, XPS, TPR, EXAFS and magnetic measurements have been used to determine the formation of bimetallic particles and/or alloys [3–5].

In bimetallic particles “dilution” of the active metallic component with a non-active metal decreases the “ensemble size”. The “ensemble size” model is most frequently used to explain changes in activity and selectivity when the active component is diluted by an inactive metal, whereas significant electronic interactions can be expected when two active components are in close contact [6]. Nevertheless, it is important to keep in mind that electronic and geometric influences cannot be considered as independent parameters. For example, Coq and Figueras pointed out that the increase in metal particle size not only increases the electron band-width and decreases the binding energies of core electron, but the nature of the exposed planes and the topology of the surface sites also changes [1]. Even in those situations in which dilution of the active sites predominate, the dilution of the active metal by a second component results in the appearance of discrete levels in the valence band and in many cases, the rehybridization of the orbitals [1].

The catalytic effect of bimetallic catalysts is also influenced by particle size and dispersion [7–12]. It is well known that the interface between metal particles and the support in-

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creases by decreasing the metal particle size. Partial electron deficiency might be created on the metal due to metal–support interaction. Quoting Guzzi and Kiricsi [8], zeolites exhibit several advantages for the preparation of small metallic or bimetallic particles since metallic or bimetallic precursors can be localized topographically. Also, the small particle size is associated with zeolite shape selectivity and acid–base properties. An important feature in the use of zeolites versus inorganic oxides as carriers is the geometrical constraint responsible for the limited particle growth due to particle confinement in the channels or cages of the zeolite [8].

The addition of a second metal could alter the electronic structure of a given supported metal, mainly when both metals are reduced forming an alloy. Nonetheless, interaction is also important when one of the metals is easily reduced and the other stays in a low oxidation state. In this case, the addition of a second metal can have a promoting effect leading to direct or indirect interaction of the difficult to reduce metal with the reacting molecule or can prevent active metal migration [8]. The addition of a second metal could modify metal dispersion. A mixed oxide phase could be formed preventing surface mobility of both metals and increasing dispersion of the active metal. Other alternative may be the formation of an oxide interface between the support and the active metal, leading to stabilization of high metal dispersion. High metal dispersion could diminish deactivation of supported metal catalysts. As a result of the enhanced dispersion there is an increase of defect sites, kinks, steps, edges and corners, where the number of next neighbors decreases and bond strength of molecules is weakened [7–9].

Among bimetallic catalysts, Pd–Co systems are of most interest because of their superior activity and selectivity in comparison to the pure metals on several reactions, i.e. hydrogenation of 1,3-butadiene impurities in commercial *n*-butene streams [13], hydrogenation of CO [14,15], methane activation to higher hydrocarbons [15] and recently the SCR of NO_x by methane [16–24]. In this work, the general properties of bimetallic Pd–Co supported on inorganic oxides on several hydrogenation reactions are reviewed. Then, the properties of Pd–Co supported on zeolites and sulfated ceria of relevance to CH₄-SCR are also examined. We seek to arrive at a general understanding of promotion in bimetallic Pd–Co supported catalysts.

2. General properties of bimetallic Pd–Co supported on inorganic oxides

It is well established that palladium promotes the activity of supported cobalt catalysts in several hydrogenation reactions. Guzzi and coworkers [13] found that the addition of small amount of Pd (0.1–1 wt.%) to 5 wt.% Co/Al₂O₃, significantly improved the hydrogenation of 1,3-butadiene impurities in commercial *n*-butene streams. The rate of butadiene consumption increased significantly between 200 and 450 °C. These results were attributed to the formation of

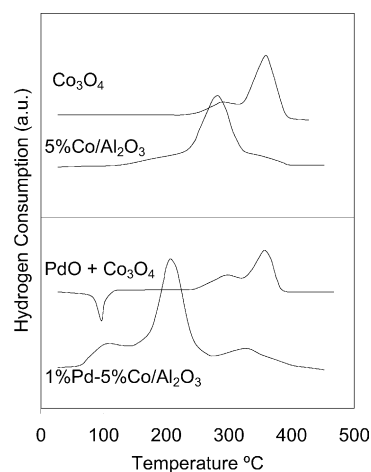


Fig. 1. Temperature-programmed reduction (TPR) profiles of unsupported Co₃O₄, alumina-supported Co₃O₄, mechanical mixtures of PdO and Co₃O₄, as well as, alumina-supported PdO–Co₃O₄ prepared by incipient wetness impregnation. Samples were calcined in flowing O₂ at 350 °C. Adapted from Ref. [13].

Pd–Co and Co ensembles rather than to the separate action of Pd and Co sites [13]. TPR profiles obtained by Guzzi and coworkers [13] of unsupported Co₃O₄, alumina-supported Co₃O₄, mechanical mixtures of PdO and Co₃O₄, as well as, alumina-supported PdO–Co₃O₄ prepared by incipient wetness impregnation are compared in Fig. 1. Unsupported Co₃O₄, was reduced in two steps at 300 and 350 °C and peak ratios are about 3. A mechanical mixture containing 11.3 wt.% Pd did not affect significantly the reduction behavior of Co₃O₄. PdO was reduced below ambient temperature and the decomposition of hydride phase appeared at 80 °C, indicating that there is some limited contact between PdO and Co₃O₄ particles. The main reduction peak for 5 wt.% Co/Al₂O₃ sample appeared at 273 °C together with small features at 180 and 350 °C. When Pd was added, the reduction peaks shifted gradually to lower temperatures.

Addition of 1 wt.% Pd to 5 wt.% Co/Al₂O₃ showed that Co₃O₄ was reduced in two steps: the first peak at 290 °C corresponds to reduction of Co³⁺ to Co²⁺ and the second peak at 350 °C to the formation of metallic Co. Furthermore, neither formation nor decomposition of hydride phase appeared after reduction indicating intimate Pd–Co interaction [13].

Schmal and coworkers studied the nature of Pd–Co interactions on graphite [3,4] and niobia [5]. They demonstrated that the formation of a solid solution decreased the adsorption strength of hydrocarbons, increasing the turnover frequencies and influencing product selectivity. Cobalt and cobalt–palladium supported on graphite samples were prepared by impregnation techniques. An intimate contact between cobalt and palladium was favorable on graphite (G) due to a weaker interaction between each of the metal precursors with the support and to a higher mobility of the supported species on graphite. Co/G catalysts were typically reduced in two steps [3]. A strong promoting effect of palladium on cobalt oxide reduction over 3.1 wt.% Pd–3.4 wt.% Co/G cata-

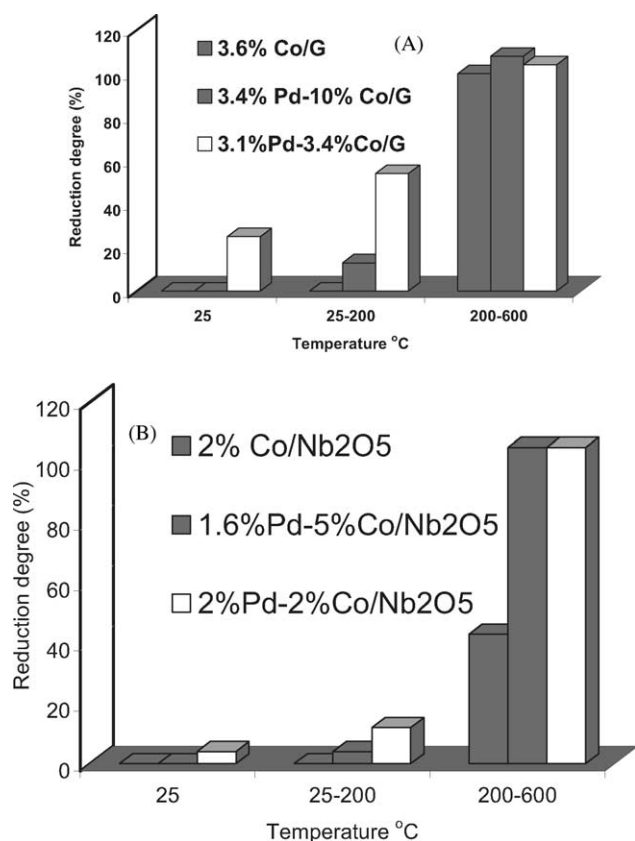


Fig. 2. Cobalt reduction degree at different temperatures calculated from magnetic measurements of Pd–Co catalysts supported on: (a) graphite, (b) niobia. Adapted from Ref. [4].

lysts, was evidenced by a shift of 152 °C in cobalt reduction. The promoting effect of palladium decreased with the increase of cobalt loading. On the other hand, since niobia promoted strong metal–support interactions (SMSI) irreducible cobalt species were formed affecting the nature of Pd–Co interactions [5]. Two weight percentage of Co/Nb₂O₅ exhibited reduction peaks at 480 and 571 °C attributed to the reduction of Co₃O₄ particles, and Co²⁺ species interacting with niobia, respectively [5]. The presence of Pd shifted the temperature of cobalt reduction between 119 and 142 °C, depending on the Co/Pd atomic ratio. Schmal and coworkers [4] also confirmed interaction between both metals by magnetic measurements at different reduction temperatures. Cobalt reduction degree of Pd–Co supported on graphite and niobia at different temperatures from magnetic measurements are compared in Fig. 2a and b [4]. Although, graphite is a less reactive support than niobia, the room temperature reducibility of cobalt was higher on graphite (25%) than on niobia (4%). The enhancement of cobalt reducibility by palladium when supported on niobia (30 m²/g) and graphite (130 m²/g) is further illustrated in Fig. 3 [3–5]. The H₂ consumption at 55 °C is higher than that expected for complete reduction of Pd. Therefore, cobalt was co-reduced with Pd at low temperature demonstrating the strong catalytic effect of palladium on the reduction of cobalt oxide. EXAFS analysis of supported

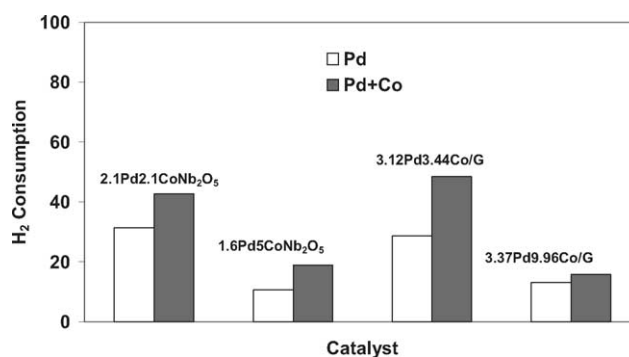


Fig. 3. Comparison between real H₂ consumption (determined from the TPR peak at 55 °C) and theoretical value expected for complete reduction of Pd in the sample. Actually Co was co-reduced with Pd. Data taken from Refs. [3–5].

niobia catalysts revealed Pd–Co alloy formation on reduced catalysts [5]. Even on Pd–Co catalysts with low cobalt content, the authors suggested the presence of bimetallic particles enriched with palladium and particles containing only cobalt. Although, XRD and HRTEM analysis of palladium–cobalt supported on graphite allowed the identification of both PdO and Co₃O₄ as separated crystallographic phases, local analysis by STEM–EDX indicated that most particles contained both metals [5]. Fig. 3 also shows that catalysts containing high Co loadings show decreased Pd reducibility. Similar results were obtained by Gucci et al. [15] who attributed discrepancies between XRD and chemisorption data concerning dispersion to encapsulation of Pd particles by Co.

It has been shown that the preparation method and the overall metal loading lead to differences in the formation of Pd–Co bimetallic catalysts [8]. Juszczak et al. [25] used two impregnation procedures to obtain Pd–Co/SiO₂ catalysts characterized by different alloy homogeneity. The first series consisted of 10 wt.% metal loaded samples, prepared by incipient wetness impregnation with careful rotary agitation during all stages of preparation. From comparison, another series containing 1 wt.% metal loading was prepared from solution with excess solvent, without any mixing. TPR analysis of SiO₂ supported Pd–Co catalysts showed that reduction of the first series (10 wt.% metal loading) was virtually complete at 380 °C while pure cobalt catalysts exhibited a reduction peak at 450 °C. On the other hand, catalysts loaded with 1 wt.% metal exhibited a quite different TPR profile. Only a very small amount of cobalt was reduced at temperatures below 800 °C. Furthermore, negative peaks indicative of hydride formation were observed suggesting that palladium did not strongly interact with cobalt. Thus, from TPR results they concluded that catalysts prepared by careful rotary agitation lead to a better homogenized Pd–Co alloy phase.

Pd–Co particles have shown improved selectivity over cobalt particles in Fischer–Tropsch synthesis to obtain long-chain hydrocarbons [14,15,26]. Synergistic effects for CO hydrogenation was observed by Gucci et al. [14] over a Pd–Co sol–gel silica supported catalyst with an atomic ratio

Co/Pd = 2. Over cobalt-supported samples short chain hydrocarbons, mainly alkenes were formed, whereas the amount of alkanes and chain length up to C₈–C₉ increased over Pd–Co silica supported catalysts. Pd–Co/SiO₂ also proved to be efficient for low temperature methane activation under non-oxidative conditions. In the presence of H₂/He, not only the production of higher hydrocarbons increased from methane dissociation, but also the selectivity shifted towards larger molecules. In contrast to the Pd–Co systems previously described, Guczi and coworkers [14] did not find bimetallic particles on sol–gel silica supported Pd–Co catalysts. Furthermore, cobalt species exhibited limited reducibility, due to the small particle size as a result of the sol–gel technique. Nevertheless, the binding energy values of Co 2p and Pd 3d obtained by XPS analysis indicated interaction between palladium and cobalt on the surface [14]. As the amount of cobalt increased, the average size of the palladium particles being in metal form, become smaller [15]. Therefore, Co appears to improve palladium metal dispersion. Tsubaki et al. also prepared silica supported Pd–Co catalysts by incipient wetness co-impregnation and found that Pd had a very positive influence on cobalt metal dispersion [26]. From EDS analysis it was concluded that well dispersed alloys with different Pd–Co compositions were formed. These results suggest intimate interactions between palladium and cobalt [26].

More recently, fundamental properties of bimetallic catalysts have been investigated using models obtained by depositing metal particles on oxide supports [27–29]. Freund and coworkers have studied morphology, grow modes, exposed binding sites, and electronic properties of Co–Pd bimetallic particles on a thin alumina film using scanning tunneling microscopy (STM), temperature-programmed desorption (TPD) of CO and X-ray photoelectron spectroscopy (XPS) [28]. In the case of pure palladium, scanning tunneling microscopy (STM) images showed that the majority of palladium particles nucleate and grow at line defects of the support and have a regular shape suggesting that they have a crystalline structure. On the other hand pure cobalt preferentially nucleates at point defects on the alumina film and there is no indication of crystalline order of the Co aggregates. Core-shell structures were formed by sequential deposition of Co and Pd. The second metal deposited formed the shell [27,28]. When Pd was deposited on a surface already covered by Co particles, it was trapped at Co particles before reaching the line defects owing to the higher mobility of Pd on the surface. On the other hand when Pd was deposited first, the less mobile cobalt atoms partly covered Pd crystallites and partially nucleated between them.

CO TPD profiles showed that CO binds preferentially to three-fold hollow sites on Pd whereas atop sites are more favored on Co [28]. The latter sites were better preserved than the former ones. Interestingly, the binding energy of CO in the three-fold hollow sites decreased with decreasing total amount of Pd, due to the electronic influence of underlying Co atom (ligand effects). XPS studies indicated that the binding energy shift of CO was not dependent on whether Pd or Co

was deposited first. A shift in the Pd 3d level to higher binding energy together with a shift in the Co 2p level to lower binding energy was an indication of a net charge polarization or redistribution of d-band states in bimetallic particles. These results were found to be in agreement with theoretical studies pointing out that a rehybridization of orbitals appears to be more significant than the net charge transfer between two different metals and to other theoretical studies concluding that the bimetallic bond is best described as metallic with a small degree of ionic character [28].

The effect of pretreatment of Co–Pd bimetallic particles on a thin alumina film was also studied by TPD [29]. Although hydrogen and CO adsorbed on non-oxidized cobalt particles, their adsorption was inhibited on the oxidized bimetallic and pure particles. On the other hand oxidized Pd particles adsorbed a small amount of hydrogen. These results allowed the authors [29] to suggest that oxidized Co or Co–Pd particles should be less active than unoxidized ones in CO hydrogenation. Consequently, reduction of CoO to metallic cobalt is crucial for Fisher–Tropsch reaction.

3. Pd–Co-supported catalysts for the selective catalytic reduction of NO_x by methane

Catalysts containing Pd and cobalt in zeolites have traditionally been studied with high palladium loadings in the reduced form for hydrogenation and hydrogenolysis reactions [30,31]. More recently, zeolite supported Pd–Co catalysts with low Pd/Co ratios have been shown to be more efficient and resistant than either Pd or Co loaded zeolites for the selective catalytic reduction (SCR) of NO by methane under hydrothermal conditions [16–24]. The most active catalysts are supported on MOR and ZSM-5 [23]. Several pretreatment conditions namely oxidant, reducing and inert atmosphere have been used. Previous reports indicate that Pd–Co/H-ZSM-5 (0.4 wt.% Pd, 3.3 wt.% Co) prepared by sequentially exchanging Pd²⁺ and Co²⁺ exhibits a stable NO conversion at 500 °C for more than 40 h in a mixture containing 0.01% NO, 0.2% CH₄, 10% O₂, 10% H₂O, space velocity 30,000 h⁻¹ [18]. Catalysts were calcined in flowing 20% oxygen at 500 °C before catalytic tests. The stable performance was explained in terms of the high stability of the active sites i.e. Co²⁺ stabilized isolated Pd²⁺ cations and their sittings in the cavities of ZSM-5 [20]. These authors also found similar Co²⁺ and Pd²⁺ interactions in a Pd–CoMOR catalyst [20]. Therefore, intimate sitting of isolated Co²⁺ in zeolite cavities stabilized the highly mobile isolated Pd²⁺ [20].

Sachtler and coworkers demonstrated synergism of cobalt and palladium in MFI zeolite [21]. They prepared MFI supported bimetallic catalysts with high Co/Pd atomic ratios by combining sublimation of a volatile cobalt compound followed by conventional ion exchange of palladium. Best performance for NO (0.1%) reduction with CH₄ (0.2%) in the presence of 2% O₂ was obtained when the catalyst Co/Pd = 14/1 was reduced in flowing H₂ before catalytic runs.

Although the N_2 yield over the above catalyst was twice that obtained over Co/MFI at 500°C and a space velocity of $90,000\text{ h}^{-1}$, no results in the presence of water vapor were reported. TPR experiments showed that the reduction of Co was significantly enhanced by the presence of small amounts of Pd in ZSM-5 [21]. The presence of Pd decreased the reduction temperature of isolated Co^{2+} ions by 190°C . The high dilution of the Pd precursor with Co ions delayed the reduction of Pd up to 45°C . As the presence of Pd favored the formation of Co^0 it was assumed that some particles look like “cherries” containing a Pd “kernel” surrounded by a Co shell. By EXAFS results they demonstrated that a thin layer of Co–Pd alloy formed along the interface between both phases. Three kinds of particles between 40 and 100 nm were detected by TEM and EDX: large Pd-rich alloy particles, small Co-rich alloy particles, and small particles of pure Co. The high and stable CH_4 -SCR activity at 300°C was ascribed to the presence of Co–Pd alloy in Co_{14}Pd previously reduced at 800°C . However, the Co–Pd alloy transformed to catalytically inactive particles in the $\text{NO}-\text{CH}_4-\text{O}_2$ feed at temperatures higher than 300°C [21].

Pieterse et al. [22] reported that Co/Pd-HZSM-5 (0.4 wt.% Pd, 2.5–2.8 wt.% Co) catalysts in which palladium was incorporated by wet ion-exchange and Co by pore volume impregnation, lead to active catalytic systems for CH_4 -SCR in the presence of water. Before tests, catalysts were calcined at 450 or 550°C . The feed consisted of 0.05% NO, 0.25% CH_4 , 5% O_2 and 5% H_2O in nitrogen, space velocity $20,000\text{ h}^{-1}$. After about 30 h time on stream (TOS) deactivation due to temperature-induced mechanism of ion migration and sintering was confirmed by TPR analysis. The deactivation was found to be almost independent of the presence of cobalt. In a further study, the authors reported the influence of the zeolite structure on the activity and stability of the Co–Pd catalysts for CH_4 -SCR [23]. ZSM-5, MOR, FER and BEA supported Pd–Co catalysts were tested in a reaction mixture containing 0.05% NO, 0.25% CH_4 , 5% O_2 and 5% H_2O in nitrogen, space velocity $20,000\text{ h}^{-1}$ at 450°C . MOR based catalysts exhibited the highest SCR activity up to about 50 h TOS under wet conditions. The activity was ascribed to well dispersed Pd^{2+} cations able to activate methane [23]. Nonetheless, characterization of spent samples indicated disappearance of metal cations, formation of inactive metal oxides and presumably larger entities leading to lower dispersion. Also, their catalysts lost crystallinity and dealuminated in the wet feed.

Except for the work of Sachtler and coworkers in which the active catalysts were those pretreated in H_2 [21] most Pd–Co zeolite supported catalysts have been treated in air or O_2 before CH_4 -SCR runs. In contrast to these studies, our Pd–Co/HMOR samples have been pretreated in flowing He at 500°C for the CH_4 -SCR under wet conditions [24,32]. The addition of 0.15 wt.% Pd by incipient wetness impregnation to Co-HMOR (4.5 wt.% Co) leads to a Pd/Co-HMOR catalyst converting 60% NO to N_2 at 500°C . The reaction mixture contained 0.1% NO, 0.27% CH_4 , 6% O_2 and 8% H_2O , space velocity $30,000\text{ h}^{-1}$. We found no significant differences on

the activity of Pd–Co supported mordenite catalysts when Pd was introduced by ion exchange instead of impregnation [32]. These results are in agreement with Loughran and Resasco [33] who demonstrated that PdO transformed into a highly dispersed state such as Pd^{2+} when supported on an acidic support. Besides, computational studies by Bell and coworkers [34] showed that Al sites facilitate the stabilization of palladium species. By deconvolution of the 3610 cm^{-1} FT-IR band we estimated that the amount of acid sites in the main channels of MOR remained constant whereas those in the side pockets decreased when Pd was added to Co-HMOR [32]. Therefore, Pd^{2+} cations in Pd/Co-HMOR appear to be preferentially located in the side pockets. UV–vis experiments showed that the relative population of Co^{2+} in the side pockets of fresh samples of Co-HMOR and Pd/Co-HMOR was higher than 80% [32]. Therefore, interactions between Pd^{2+} and Co^{2+} might occur mainly in the lateral channels of mordenite.

Interestingly, although Pd–Co interactions have been found in alumina-supported Pd–Co catalysts, they are not active for CH_4 -SCR [24]. Therefore, acidity plays an important role on the SCR of NO_x . It contributes to position Co^{2+} and Pd^{2+} at exchange positions of zeolites [24] leading to high metal dispersion. In the same way, sulfated zirconia (SZ) is able to promote the NO reduction activity similar to acid zeolites by stabilizing Pd^{2+} and Co^{2+} ions [35,36]. We have recently found that a Pd/Co-SZ catalyst exhibits remarkable performance under lean conditions and displays stability in long-term durability tests in the presence of steam at 550°C [37]. The reaction mixture contained 0.1% NO, 0.3% CH_4 , 5% O_2 , and 10% H_2O , space velocity $45,000\text{ h}^{-1}$. Catalyst samples were prepared by impregnating a sol–gel Co-SZ material (2.14 wt.% Co) with 0.06 wt.% Pd (Pd/Co-SZ-2). Before the experiments the catalysts were pretreated 4 h in He at 500°C . Pretreatment of Pd/Co-SZ samples in flowing helium, probably lead to partial reduction of sulfate and stabilization of cobalt species as cobalt sulphite (CoSO_3) [37].

H_2 -TPR profiles of Co and Pd/Co fresh and aged catalysts supported on mordenite [32] and sulfated zirconia [37] are compared in Fig. 4. Although both catalysts exhibit similar features, sulfated zirconia promotes cobalt reduction at lower temperatures as compared to mordenite. Fresh and aged Pd/Co catalysts supported on MOR and SZ, show no negative reduction peaks from hydrides suggesting that the size of Pd particles are in the nanometer scale [1]. The peak at 220°C in the TPR profile of Co-HMOR was ascribed to Co oxo-ions and the main peak of cobalt reduction shows up at 944°C with a shoulder at 839°C [24]. These features have been assigned to the reduction of Co^{2+} ions at exchange positions in the mordenite side pockets, and in the 12-member ring channels, respectively [24]. The temperatures at which Co^{2+} ions are reduced in Co-HMOR are lowered to 900 and 719°C in fresh Pd/Co-HMOR. TPR profiles of Co-SZ samples exhibit two reduction features. The high temperature peak, assigned to reduction of sulfate, is shifted to lower temperature by more than 120°C in comparison to SZ (not shown) [37]. The

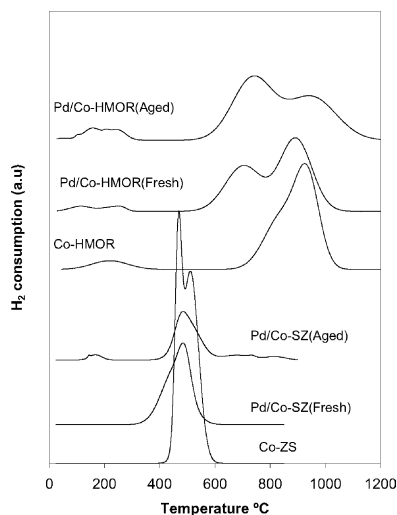


Fig. 4. H₂-TPR profiles of Co-HMOR, Pd/Co-HMOR (fresh and aged samples) and Co-SZ, Pd/Co-SZ (fresh and aged samples). All samples were calcined at 500 °C before TPR measurements.

peak at 467 °C is attributed to reduction of Co²⁺ [38]. Similar to platinum [39] and Fe [40], Co promotes the reduction of sulfate groups so a significant fraction of cobalt must be present as Co⁰ or as cobalt sulfide capable to dissociate H₂ molecules. Pd/Co-SZ-2 exhibits a broad peak with a shoulder at 430 °C assigned to Co²⁺ which shifted to lower temperature in comparison to Co-SZ.

Similar to what has been observed with other supports [3–5,13–15,26], the temperature required to reduce Co²⁺ is lowered by the presence of Pd in Pd/Co-HMOR and Pd/Co-SZ. However, in the aged samples, those peaks are shifted to higher temperatures and new features at low temperature (110–250 °C) ascribed to cobalt oxide and Co oxo-ions appear in Pd/Co supported mordenite and sulfated zirconia, respectively. Pd/Co-SZ-2 samples were selective and stable for the CH₄-SCR about 35 h TOS. FT-IR, TPR and chemical analysis of spent samples suggested that the main cause of deactivation of Pd/Co-SZ-2 is sulfate loss, probably as SO₂, with the consequent decrease in the ability to stabilize cationic species [37].

Pd/Co-HMOR exhibited an exponential deactivation pattern typical of the disappearance of active sites. However, this catalyst still converted about 40% NO_x for more than 100 h TOS at 500 °C, space velocity 12,000 h⁻¹ in a wet stream [32]. FT-IR, ²⁷Al NMR and ²⁹Si MAS NMR confirmed steam-induced dealumination in the 12-ring channels, but the side pockets appeared to be less affected [32]. By ¹²⁹Xe NMR, Kneller et al. also determined that the side pockets of MOR do not seem to be affected by the dealumination process [41]. Therefore, close interaction between Pd²⁺ and Co²⁺ in the 8-ring channels of MOR may be the reason for the relative high stability of Pd/Co-HMOR under wet conditions at long TOS.

Sachtler and coworkers noticed that both Pd and Co zeolites use the zero valent state of the metal in their redox couple

and are able to reduce NO_x by methane [42–45]. Therefore, they postulated that Co⁰ or Pd⁰ atoms provide the sites on which methane is activated by dissociative chemisorption. Pd²⁺ cations in Pd zeolites are easily reduced to Pd⁰ in one step [46]. By H/D exchange of methane, Wen and Sachtler demonstrated that in the steady state of NO reduction by methane over Pd/MFI some Pd⁰ exists, even in the presence of excess oxygen, indicating that NO and CH₄ can act as effective reductants of Pd²⁺, oxo-ions or PdO [47]. These authors suggested that the same may apply to Co/MFI. Notwithstanding, since isolated Co²⁺ species need high temperature to be reduced to Co⁰ in a single step [47], the amount of Co⁰ in the same reaction mixture should be lower than that of Pd⁰. Although there is a major advantage of using Pd and Co together in a zeolite support due to the increased reducibility of Co by the addition of Pd, the improved resistance to steam over Pd/Co-HMOR or Pd/Co-SZ during the lean CH₄-SCR probably relies on the high Pd dispersion brought about by the support acidity (MOR or SZ) or dilution and stabilization by Co²⁺ cations. In the case of Pd/Co-HMOR, the fact that residual organics from precursors were removed in flowing He, lead us to speculate that a finite concentration of small zero-valent palladium and/or cobalt might be present in the lateral channels of MOR which are responsible for methane activation. Since no hydrides were observed in TPR of Pd/Co-HMOR and Pd/Co-SZ, the particle size of Pd appears to be in the nanometer scale range. Therefore, small and highly dispersed Pd and/or Co particles appear to be crucial for the lean CH₄-SCR.

4. Concluding remarks

Several observations confirm the positive effect of Pd addition to cobalt-supported catalysts. Under reducing atmospheres:

- Cobalt can be co-reduced with Pd.
- No hydride phase is formed or decomposed after reduction.
- There is positive influence of Pd on cobalt metal dispersion and vice versa.
- There is a decrease on the adsorption strength of hydrocarbons leading to an increase of the turnover frequencies influencing product selectivity.

Under the steady state lean NO reduction with methane:

- Low Pd loadings promote the activity and durability of Co-HMOR and Co-SZ in the presence of steam, provided catalyst pretreatment is carried out under conditions which favor small and highly dispersed Pd and/or Co particles.

Acknowledgements

The authors are grateful to UdeA and CYTED program (Project V.7) for supporting this work. LFC acknowledges a

doctoral fellowship from COLCIENCIAS and the research support and advice of Professor Wolfgang Sachtler during his stay at the Environmental Catalysis Center in Northwestern University (USA). This review article was elaborated around the Third San Luis Symposium on Surfaces, Interfaces and Catalysis held at Mérida-Venezuela (March 15–19, 2004). We acknowledge the organizers for the opportunity to participate with this invited lecture.

References

- [1] B. Coq, F. Figueras, *J. Mol. Catal. A* 173 (2001) 117.
- [2] J.A. Rodríguez, *Surf. Sci. Rep.* 24 (1996) 223.
- [3] F.B. Noronha, M. Schmal, C. Nicot, B. Moraweck, R. Fréty, *J. Catal.* 168 (1997) 42.
- [4] F.B. Noronha, M. Schmal, R. Fréty, C. Bergeret, B. Moraweck, *J. Catal.* 186 (1999) 20.
- [5] F.B. Noronha, M. Schmal, B. Moraweck, P. Delichere, M. Brun, F. Villain, R.J. Fréty, *J. Phys. Chem. B* 104 (2000) 5478.
- [6] R.W. Joyner, E.S. Sphiro, P. Johnston, G.J. Tuleova, *J. Catal.* 141 (1993) 250.
- [7] L. Guzzi, D. Bazin, *Appl. Catal. A* 188 (1999) 163.
- [8] L. Guzzi, I. Kiricsi, *Appl. Catal. A* 186 (1999) 375.
- [9] L. Guzzi, Gemmin Lu, A. Zsoldos, *Catal. Today* 17 (1993) 459.
- [10] L. Guzzi, R. Sundararajan, As. Koppány, Z. Zsoldos, Z. Schy, F. Mizukami, S. Niwa, *J. Catal.* 167 (1997) 482.
- [11] L. Guzzi, L. Borkó, Z. Schay, D. Bazin, F. Mizukami, *Catal. Today* 64 (2001) 91.
- [12] Z. Zsoldos, G. Vass, G. Lu, L. Guzzi, *Appl. Surf. Sci.* 78 (1994) 467.
- [13] A. Sárkány, Z. Zsoldos, Gy. Stefler, J.W. Hightower, L. Guzzi, *J. Catal.* 157 (1995) 179.
- [14] L. Guzzi, Z. Schay, G. Stefler, F. Mizukami, *J. Mol. Catal. A* 141 (1999) 177.
- [15] L. Guzzi, L. Borkó, Z. Schay, D. Bazin, F. Mizukami, *Catal. Today* 65 (2001) 51.
- [16] C. Hamon, O. Le Lamer, N. Morio, J. Saint-Just, US Patent 60,630,351 (1998).
- [17] M. Ogura, Y. Sugiura, M. Hayashi, E. Kikuchi, *Catal. Lett.* 42 (1996) 185.
- [18] M. Ogura, S. Kage, M. Hayashi, M. Matsukata, E. Kikuchi, *Appl. Catal. B* 27 (2000) 213.
- [19] F. Bustamante, P. Avila, C. Montes de Correa, in: A. Galarneau, F. Di Renzo, F. Fajula, J. Vedrine (Eds.), *Studies in Surface Science and Catalysis*, vol. 138, Elsevier, Amsterdam, 2001, p. 325.
- [20] M. Ogura, S. Kage, T. Shimojo, J. Oba, M. Hayashi, M. Matsukata, E. Kikuchi, *J. Catal.* 211 (2002) 75.
- [21] B. Wen, J. Jia, S. Li, T. Liu, L.X. Chen, W.M.H. Sachtler, *Phys. Chem. Chem. Phys.* 4 (2002) 1983.
- [22] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, *Appl. Catal. B* 39 (2002) 167.
- [23] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, *Appl. Catal. B* 46 (2003) 239.
- [24] F. Bustamante, F. Córdoba Castrillón, M. Yates, C. Montes de Correa, *Appl. Catal. A* 234 (2002) 127.
- [25] W. Juszczyk, Z. Karpinski, D. Lomot, J. Pielaszek, Z. Paal, A.Yu. Stakheev, *J. Catal.* 142 (1993) 617.
- [26] N. Tsubaki, S. Sun, K. Fujimoto, *J. Catal.* 199 (2001) 236.
- [27] M. Heemeier, A.F. Carlsson, M. Naschitzki, M. Schmal, M. Baumer, H.-J. Freund, *Angew. Chem. Int. Ed.* 41 (2002) 4073.
- [28] A.F. Carlsson, M. Naschitzki, M. Bäumer, H.-J. Freund, *Surf. Sci.* 545 (2003) 143.
- [29] A.F. Carlsson, M. Naschitzki, M. Bäumer, H.-J. Freund, *J. Phys. Chem. B* 107 (2003) 778.
- [30] Z. Karpinski, Z. Zhang, W.M.H. Sachtler, *Catal. Lett.* 13 (1992) 123.
- [31] Z. Zhang, W.M.H. Sachtler, *J. Chem. Soc., Faraday Trans.* 86 (1990) 2313.
- [32] L.F. Córdoba, G.A. Fuentes, C. Montes de Correa, *Micropor. Mesopor. Mater.*, in press.
- [33] C. Loughran, D.E. Resasco, *Appl. Catal. B* 7 (1995) 113.
- [34] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, *J. Catal.* 172 (1997) 453.
- [35] Y.-H. Chin, A. Pisanu, L. Serventi, W.E. Alvarez, D.E. Resasco, *Catal. Today* 54 (1999) 419.
- [36] N. Li, A. Wang, J. Tang, X. Wang, D. Liang, T. Zhang, *Appl. Catal. B* 43 (2003) 195.
- [37] L.F. Córdoba, W.M.H. Sachtler, C. Montes de Correa, *Appl. Catal. B*, in press.
- [38] B. Wen, J. Jia, S. Li, T. Liu, L.X. Chen, W.M.H. Sachtler, *Phys. Chem. Chem. Phys.* 4 (2002) 1983.
- [39] B.-Q. Xu, W.M.H. Sachtler, *J. Catal.* 167 (1997) 224.
- [40] W.M.H. Sachtler, Personal communication.
- [41] J.M. Kneller, T. Pietrab, K.C. Ott, A. Labouriau, *Micropor. Mesopor. Mater.* 62 (2003) 121.
- [42] B.J. Adelman, W.M.H. Sachtler, *Appl. Catal. B* 14 (1997) 1.
- [43] B. Wen, Q. Sun, W.M.H. Sachtler, *J. Catal.* 204 (2001) 314.
- [44] X. Wang, H.Y. Chen, W.M.H. Sachtler, *Appl. Catal. B* 26 (2000) 227.
- [45] X. Wang, H.Y. Chen, W.M.H. Sachtler, *Appl. Catal. B* 29 (2001) 47.
- [46] X. Wang, H.Y. Chen, W.M.H. Sachtler, *J. Catal.* 197 (2001) 281.
- [47] B. Wen, W.M.H. Sachtler, *Appl. Catal. A* 229 (2002) 11.