Journal of Catalysis 309 (2014) 439-452

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Highly selective direct amination of primary alcohols over a Pd/K-OMS-2 catalyst



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ARTICLE INFO

Article history: Received 21 July 2013 Revised 16 September 2013 Accepted 7 October 2013

Keywords: Direct amination Borrowing hydrogen Heterogenous catalyst OMS-2 Doping

ABSTRACT

A new Pd-substituted octahedral molecular sieve (Pd/K-OMS-2) catalyst has been prepared for the direct amination of alcohols with primary amines operating under the borrowing hydrogen mechanism. The catalyst offered full conversion and high selectivity toward N-benzylaniline in the model alkylation reaction of aniline with benzyl alcohol at mild temperature (160 °C) for 3 h with neither production of the tertiary amine nor toluene. Pd/K-OMS-2 performed as a tandem tri-functional catalyst, first oxidizing benzyl alcohol to benzaldehyde, behaving as a Lewis acid for imine formation, and finally reducing the imine to the secondary amine. The catalyst was characterized in depth using BET, XRD, H₂-TPR, XPS, FTIR, TEM, TGA/DTG, and ICP-AES / EDX to elucidate the nature of the active sites. The unexpectedly high performance of the Pd/K-OMS-2 catalyst can be ascribed, at least partially, to the *in situ* generation of a very active, selective and partially recyclable Pd-substituted/supported hausmannite phase (i.e., Pd/Mn₃O₄) in the early stage of the reaction with a high density of surface oxygen moieties. We argue about a possible role of a Pd(IV)/Pd(II) redox pump for exchanging hydrogen during the amination reaction.

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1. Introduction

Amines are key chemical intermediates widely used as building blocks for the synthesis of polymers, dyes, pharmaceuticals, and agrochemicals [1]. The industrial synthesis of amines usually involves hazardous reagents (e.g., HCN) or generates hazardous byproducts (e.g., HCl). Moreover, the preparation of primary amines by direct nucleophilic substitution of organic halides suffers most often from a lack of selectivity, the reaction usually rendering a mixture of primary, secondary, and tertiary amines. The use of acid catalysts to activate the alcohol group can also be responsible for the generation of alkenes through uni/bimolecular elimination mechanisms [2]. An alternative process based on the addition of ammonia or amines on alkenes has also been proposed for the synthesis of tertiary amines over acid catalysts (e.g., t-butylamine from isobutene), but with limited selectivities [3]. Finally, amines can also be produced by the reduction of amides, but generally under harsh conditions [4].

Recently, transition metal complex-catalyzed direct N-alkylation of amines and ammonia with alcohols has been reported as an alternative route to amines through the so-called borrowing hydrogen or hydrogen auto-transfer mechanism [5–7], encompassing a net transfer of H_2 from the alcohol to the intermediate imine. As in reductive amination of carbonyls, the amination

* Corresponding author. *E-mail address:* marc.pera-titus-ext@solvay.com (M. Pera-Titus). reaction proceeds via an intermediate imine or enamine affording only water as by-product [3]. Nonetheless, unlike reductive amination, no additional reductive species (usually H₂) is required for imine or enamine hydrogenation. The borrowing hydrogen mechanism overcomes the lack of reactivity of reductive amination catalysts (most often based on Ni and NiCuMg formulations) by the temporary removal of "H₂" from the alcohol by the catalyst to give a carbonyl, which is more reactive toward the amine or ammonia. The catalyst returns the "borrowed H₂" by reducing the imine into the alkylated amine product.

The first studies on heterogeneous catalytic formulations for alcohol amination via the borrowing hydrogen mechanism focused on Ni-Raney [8,9] and Ni and Co nanoparticles supported on silica and alumina [10–15]. However, as in reductive amination, the reaction was carried out under H₂ atmosphere to maintain the activity of the catalyst. The introduction of small amounts of noble metals on Ni and Co catalysts (typically 15-20% Ni or Co + 0.5-3% Pd on alumina, silica, or titania) was shown to enhance the catalytic activity and reduce the activation temperature [16]. Unsupported Co-Fe catalysts prepared by co-precipitation [17,18], and Cu/Ni/Ca/Ba colloidal mixed-oxide catalysts prepared from stearate precursors exhibited selectivity for the synthesis of primary diamines from diols in (supercritical) ammonia [19]. Furthermore, Baiker and co-workers [20] prepared Co-Fe catalysts based on Fe/Co₃O₄ with β -Co metal cluster sites for the amination of 1,3-propanediol with ammonia in the pressure range 50-150 bar. The absence of strong acidic and basic sites was





JOURNAL OF CATALYSIS

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claimed as crucial for suppressing acid/base-catalyzed side reactions (e.g., retro-aldol reaction, alkylation, disproportionation, dimerization, and oligomerization). A small amount of Fe additive could efficiently hinder the transformation of β -Co into α -Co phase and prevent catalyst deactivation.

More recent examples include Ni, Cu, and NiCu supported on silica and alumina [21,22] and iron oxide [23] for amination reactions of aromatic amines and alcohols. In the case of aliphatic systems, high yields have been recently reported on CuAl/hydrotalcite $(+K_2CO_3 \text{ additive})$ [24] and CuNi/ γ -Al₂O₃ [25] formulations at 160 °C for 9–12 h under air or N₂ atmosphere, the latter catalysts showing yields >70% toward the secondary amine. In the case of supported noble metals, Au/MgO [26], Au/TiO₂ [27], and Au/ZrO₂ [28,29] catalysts showed a moderate capacity for imine formation by promoting alcohol deprotonation in the first step of the reaction, but low capacity for amine formation. The combined dehydrogenation capacity of metal nanoparticles (mean size < 3 nm) with the aniline and benzyl alcohol adsorption capacity of the support via Brønsted basic and Lewis acid sites, respectively, was argued as crucial for promoting secondary amine formation [28]. Partially active and selective formulations based on Ag were reported by Shi et al. [30] over Ag–MoO_x oxides and by Jaenicke and co-workers [31] over alumina-entrapped Ag nanoparticles doped with Cs₂CO₃. Heterogeneous bimetallic Pt–Sn/ γ -Al₂O₃ catalysts (Pt with SnO₂) showed activity in the direct synthesis of secondary and tertiary diamines from the reaction of aliphatic diols with aniline [32].

Ru- and Pd-based catalysts have shown the most promising potentials for the amination of alcohols. On the one hand, liquidphase amination of cyclohexanol over a Ru/Al₂O₃ catalyst in a batch reactor was reported to generate cyclohexylamine with high selectivity [33,34], whereas Ru(OH)_x/Al₂O₃ [35] and Ru(OH)_x/TiO₂ [36] catalysts demonstrated the N-alkylation of alcohols via the preferential alcohol adsorption on weakly basic/acid Al-OH and Ti-OH sites. On the other hand, Shi and co-workers prepared a Pd/Fe₂O₃ catalyst by co-precipitation and further calcination, achieving full conversion and selectivity to the secondary amine at 160 °C in the reaction of aniline with benzvl alcohol [37]. The authors claimed that the active species consisted of a mixture of Pd(IV) and Pd(II) moieties activated by the support. Corma and co-workers [38] reported promising yields to N-phenyl benzyl amine in the reaction of benzyl alcohol with aniline at 180 °C at short times (<2 h) using Pd(0.8-5 wt.%)/MgO basic catalysts. The initial reaction rate was found to increase inversely with the Pd nanoparticle size (mean size < 5 nm) with a partial role of the support in stabilizing hydride species.

In this study, we concentrate our attention on metal-doped cryptomelane-type manganese oxide Octahedral Molecular Sieves (OMS-2) as potential candidates for amination reactions. OMS-2 materials (also termed K-hollandites or γ -MnO₂) are based on edge-shared MnO₆ octahedra hosting both Mn(III) and Mn(IV), and 2×2 1D microtunnels incorporating ex-framework compensation cations (usually K⁺) [39]. The direct doping of OMS-2 by solid-state conversion or aqueous-phase acid synthesis can only be achieved in seldom cases, since other more stable manganese phases are usually favored [40]. The direct exchange of K⁺ by other alkaline cations is often discouraged due to the stability of the former in OMS-2, requiring most often a preliminary acid treatment at long times [41,42]. Higher exchange capacities can be achieved by the synthesis of Na-(Mg)-birnessite (OL-1) precursors with the desired metal nitrate salts (e.g., alkaline cations [43], Ag [44,45], Co [44], Cu [44], Pb [46], and Cr [47]) followed by solid-state transformation to the OMS-2 phase by hydrothermal synthesis at 120-200 °C from a few hours to a few days [43]. Framework substitution of octahedral Mn by low- and high-valent metal cations such as Ni(II) [48,49], Co(II) [48,49], Cu(II) [48–50], Zn(II) [48], Cr(III) [47,49], Fe(III) [40,49], Ti(IV) [51], V(V) [52], and W(VI)

[53] has also been accomplished with a variable extent of substitution. Finally, in addition to cation substitution, oxide/metal nanoparticles grown over OMS-2 (e.g., CuO [54], Pt [55,56], Au [57,58]) were also achieved via incipient wetness impregnation using a metal salt precursor at short contact times.

In addition to total oxidation of VOCs, doped OMS catalysts have been applied with success to partial oxidation [42,58-61], epoxidation [62], and hydrogenation [63,64] reactions. To our knowledge, the sole study on the application of the raw K-OMS-2 to the N-alkylation of aromatic and aliphatic amines was reported by Suib and co-workers [65], showing the preferential generation of imines, but with no amine formation. The reaction was carried out in the presence of an apolar solvent (toluene or o-xylene) at moderate temperature (110-140 °C) under air for in situ regeneration of the catalyst. An excess of oxygen promoted the generation of primary amides in the presence of ammonia by oxidation of the imine to an intermediate nitrile species that could be further hydrated to the final amide [66]. In a step further, here we show that a Pd-substituted K-OMS-2 formulation can be competitive for amine synthesis from an imine intermediate via a hydrogen borrowing mechanism under inert atmosphere.

2. Experimental

2.1. Materials

Manganese sulfate hydrate (MnSO₄·H₂O, 99.5%) and potassium permanganate (KMnO₄, 99.5%), both supplied by Sigma-Aldrich, were used as reactants for the synthesis of the OMS-2 phases and Mn₂O₃ and MnO₂ supports. Aerosil 200 silica (99%, Evonik), γ -Al₂O₃ (99.9%), TiO₂ (99.9%) and CuO (99.9%), the latter three oxides supplied by Sinopharm, were used as supports. Aluminum, iron, and copper nitrate salts (99.5% in all cases), all supplied by Sinopharm, were used as precursors for catalyst preparation by co-precipitation. Tetraamminepalladium (II) nitrate (Pd(NH₃)₄ (NO₃)₂, 99.99%), provided by Sigma-Aldrich, was used for Pd impregnation/substitution over the different supports or coprecipitation with other metal nitrate precursors. The Pd/C catalyst (5 wt.% Pd) was provided by Sigma–Aldrich. Aniline (99.5%), benzyl alcohol (99.5%), N-phenyl benzylimine (99.5%), N-phenyl benzylamine (99.5%), N,N-dibenzylaniline (99.5%), and biphenyl (>99%), all purchased at J&K, were used in the catalytic tests and as standards for GC calibration.

2.2. Catalyst synthesis

K-OMS-2 manganese octahedral molecular sieve was prepared by the reflux method [67]. Briefly, an aqueous solution of KMnO₄ (40 g in 680 mL deionized water) was added to a solution of MnSO₄·H₂O (54.446 g in 180 mL deionized water) and concentrated nitric acid (20 mL) in a 1-L round-bottom flask equipped with a condenser. The final mixture was refluxed at 110 °C for 24 h. Finally, the dark brown solid was washed by filtration (ϕ = 0.02 µm) with deionized water (5 L) until neutral pH and dried overnight at 120 °C. An acid OMS-2 support (labeled here as K,H-OMS-2) was prepared following the protocol above stated, but washed until pH 4.

The amorphous MnO_2 phase was prepared via the redox reaction of $KMnO_4$ and $MnSO_4 \cdot H_2O$ at room temperature. In a typical preparation, $KMnO_4$ (11.6 g in 200 mL deionized water) was added to a solution of $MnSO_4 \cdot H_2O$ (18.6 g in 60 mL deionized water) and stirred under vigorous stirring for 6 h. Finally, the dark brown solid was washed by washed and filtrated several times until neutral pH (10 L of deionized water) and dried overnight at 120 °C. The crystalline Mn_2O_3 phase obtained from the amorphous solid by heating at 700 °C for 2 h under air atmosphere.

Ru, Pd, Au, and Ag incorporation over the calcined K-OMS-2, K,H-OMS-2, MnO₂ and Mn₂O₃ samples (2.0 wt.% theoretical loading) was carried out by ion exchange using a diluted aqueous solution (10^{-4} M) of the corresponding metal precursor, M(NH₃)₄(NO₃)_x, at 80 °C for 2 h under N₂ atmosphere. Standard Pd-supported samples were prepared by the incipient wetness impregnation (IWI) and co-precipitation (CP) methods over 6 commercial supports. On the one hand, in the former method, 48 mL of $Pd(NH_3)_4(NO_3)_2$ (1.4 g/L) was added dropwise over 3 g of the corresponding support and heated at 80 °C for 2 h under N₂ atmosphere. On the other hand, the co-precipitated samples were prepared by mixing Pd(NH₃)₄(NO₃)₂ and the corresponding metal precursor, $M(NO_3)_x$, the pH of the final solution was adjusted at 11.0. The mixture was then heated at 80 °C for 2.0 h under N₂ atmosphere. After the synthesis, both the Pd-impregnated and co-precipitated samples were subjected to vacuum evaporation (150 mbar) at 70 °C, dried overnight at 100 °C, and finally calcined at 300 °C for 2 h under air. In all cases, the theoretical Pd loading of the samples was about 2.3 wt.%.

2.3. Catalyst characterization

The phases present in the different samples were analyzed by powder X-ray diffraction (PXRD). PXRD analyses were carried out using a Rigaku D/Max-2200/PC Diffractometer provided with Cu K α radiation (λ = 1.5418 Å) and a beam voltage of 45 kV. The patterns thus obtained were indexed using the Joint Committee on Powder Diffraction (JCPDS) database.

The morphology and structure of the Pd-supported manganese samples were inspected by transmission electron microscopy (HRTEM) on a JEOL JEM-2100F (200 kV) microscope equipped with energy dispersive X-ray (EDX) analysis (semiquantitative) using a Philips PV 9800 spectrometer operated under the SuperQuant software.

In addition to EDX analysis, the bulk Pd composition in the metal-supported/exchanged samples was analyzed by inductively coupled plasma (ICP-AES) on a Perkin-Elmer optical emission spectrometer (Optima 8000) equipped with an auto-sampler. Furthermore, the surface Mn, K, and Pd composition of the samples was analyzed by X-ray photoelectron analysis (XPS) on an Axis Ultra DLD spectrometer (Kratos Analytical) provided with Al K α radiation (hv = 1486.6 eV) and operating at 150 W (10 mA to 15 kV). Carbon (C1s = 284.5 eV) was used as internal standard.

The specific surface area and pore volume of the different samples were measured from N₂ adsorption–desorption isotherms at 77.4 K using a Micromeritics ASAP 2010 surface area analyzer. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method in the relative pressure range $0.05 < P/P_0 < 0.25$, while the pore volumes were measured at $P/P_0 = 0.99$. The Barret–Joyner–Halenda (BJH) method was used for measuring intercrystalline mean pore sizes. The *t*-plot method was used to measure the external surface of the catalysts and micropore volume. Prior to the measurements, the silica samples were degassed at 200 °C under vacuum (0.5 mbar) during 15 h.

Thermogravimetric analysis (TGA) was employed to study the thermal behavior of the samples. The experiments were performed on a TA SDT Q600 Instrument. The samples were heated from room temperature to 1400 °C at a rate of 5 °C/min both under N₂ and air atmosphere (100 mL(STP)/min). The heat flow data were dynamically normalized using the instantaneous weight of the sample at the respective temperature.

H₂-TPR profiles were collected on a Micromeritics AutoChem II2920 system equipped with a quartz U-type tubular reactor and a TCD detector. A cold trap was used before the detector to avoid any interference of water in the TPR plot. In each test, 50 mg of the sample was loaded into the reactor and purged with 30 mL/ min He at 300 °C for 1 h to remove adsorbed moisture and vapors and then cooled down to room temperature. The temperature was then increased up to 750 °C at a heating rate of 10 °C/min under a H₂ flow diluted in Ar (10 v/v%). The system was calibrated using an Ag₂O standard (>99% purity) to measure the amount of H₂ consumed in the TPR tests.

Infrared spectra of the materials were recorded on calcined powders dispersed in KBr (2 mg sample in 300 mg KBr) using a Perkin-Elmer One FTIR spectrometer with a resolution of 4 cm⁻¹ operating in the range 500–2000 cm⁻¹ with 4 scans per spectrum.

2.4. Catalytic tests

The catalytic activity of the different Pd-impregnated catalysts was investigated in the model amination reaction of benzyl alcohol with aniline (Fig. 1). The reaction was performed using 2 mmol of aniline (A) and 6 mmol of benzyl alcohol (BA) and 60 mg of catalyst in a Radley's multicell reactor under N₂ or air atmosphere at 160 °C for 3 h and stirring speed of 600 rpm. The reactants (aniline and benzyl alcohol) and expected products, i.e. (a) N-phenylbenzylimine (PBI), (b) N-phenylbenzylamine (PBA), and (c) N,N-dibenzylaniline (DBA), were analyzed and quantified using an Agilent 7890 GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups using biphenyl as internal standard. Mass balances were accurate to within 5% in all the catalytic tests.

3. Results

3.1. Catalyst screening

A first series of metal-doped OMS-2 (2.3 wt.% metal loading) catalysts was prepared to assess for the effect of noble metals on the catalytic performance. Fig. 2 collects the results obtained in terms of aniline conversion and yields to PBI and PBA under N₂ atmosphere. Fig. 2 also includes a blank test, indicating a very small yet detectable conversion of aniline into PBI (<3%) in the absence of catalyst. In line with the results reported by Suib and coworkers [65], despite the notable activity endowed by the raw K-OMS-2 (ca. 47% aniline conversion), only the imine product (i.e., PBI) was formed, suggesting an inefficient hydrogen transfer from the catalyst to the imine. A similar type of effect was observed on Pt/ and Au/K-OMS-2 with no amine formation. A different picture was observed for the Ru-, Ag-, and Pd-doped K-OMS-2 and Pd/K,H-OMS-2 samples, showing a partial PBA formation and



Fig. 1. Model amination reaction of aniline and benzyl alcohol for catalyst screening (a = PBI, b = PBA, c = DBA).



Fig. 2. Summary of aniline conversions and PBI and PBA yields obtained for the reaction of BA with A over modified X/Y-OMS-2 catalysts, where X = Pd, Pt, Au, Ru, Ag or – and Y = K and/or H. For comparison, a blank experiment is also included. *Conditions*: 1:3 A/BA molar mixture, 160 °C, 3-h reaction, N₂ atmosphere, 60 mg catalyst (2 wt.% X loading).

comparatively higher aniline conversions. Among these formulations, Pd/K-OMS-2 offered the best catalytic performance, reaching 99% aniline conversion and a PBA yield as high as 96% with the sole formation of PBI (3%) as by-product (neither DBA nor benzene/toluene was detected after reaction). The catalytic performance was, however, affected by the acid-base properties of OMS-2. Indeed, partial acidification of the sample decreased the PBA yield down to 70% while keeping the aniline conversion essentially unmodified.

Given the promising performance of the Pd/K-OMS-2 formulation, we decided to carry out a comparative study on other Pdexchanged manganese oxides (i.e., amorphous MnO₂ and Mn₂O₃) and on standard Pd-supported catalysts prepared both by the IWI and CP methods. In most cases, Pd incorporation by impregnation afforded the genesis of samples with improved aniline conversions and PBA yields than the co-precipitated counterparts (ESI, Fig. S1), most likely due to a better dispersion of the Pd phase on the support after calcination. Only two exceptions were found for the co-precipitated Pd/Fe₂O₃ and Pd/CuO systems, the former offering full aniline conversion and a PBA yield as high as 96% in good agreement with the results reported by Shi and co-workers [37]. The former sample displayed well-dispersed Pd nanoparticles around 10 nm with some larger particles about 50 nm (not shown). According to this body of results, we decided to concentrate our further attention on ion exchange and IWI as strategies for the design of Pd-modified/supported amination catalysts.

Table 1 compiles the main physical and textural characteristics of the most active and selective Pd-exchanged manganese oxides and Pd-impregnated formulations found in this study in the alkylation reaction of aniline with benzyl alcohol (PBA yield > 30%). For the sake of comparison, Table 1 also includes the results reported by Shi and co-workers [37] and Corma and co-workers [38], respectively, over Pd/Fe₂O₃ and Pd/MgO catalysts taken as benchmark systems. Regardless of the acid–base and redox nature of the supports, the different catalytic formulations offered partial selectivity to the secondary amine (PBA) at reasonable aniline conversions. The tertiary amine (DBA) and other by-products (e.g., benzene and toluene) were also detected, but at very low yields. In all cases, the different formulations offered a competitive performance compared to the benchmark Pd/Fe₂O₃ and Pd/MgO formulations at similar Pd loading (ca. 2 wt.%).

As a general trend, Pd-impregnated samples based on supports with a moderate basic or amphoteric behavior (i.e., K-OMS-2, Mn₂O₃, Al₂O₃, Fe₂O₃) offered higher PBA yields, but with no straightforward correlation with neither their redox nature nor specific surface (Table 1). Among the different samples, Pd/K-OMS-2 offered the best aniline conversion and PBA yields. Encouraged by these results, we decided to conduct a complete study on this catalyst not only to assess its performance, but also to rationalize the nature of the active sites with special insight into the subtle interplay between Pd moieties and basic sites. These aspects are tackled in detail below.

3.2. Catalytic performance of Pd/K-OMS-2

3.2.1. Reaction kinetics

Additional tests were carried out to investigate the effect of the reaction time on the reactivity of the Pd/K-OMS-2 catalyst. The tests were carried out at standard reaction conditions (*vide supra*) for 1, 3, and 6 h (Fig. 3). On the one hand, the aniline conversion increased from 86% after 1 h to reach 100% after 3 h and beyond. On the other hand, the PBI yield decreases from a value of 12% after 1 h reaction down to 3% after 3 h and vanished after 6 h, whereas the PBA yield increased from 73% to 93% when the reaction time evolved from 1 to 3 h and became stable at 99% after 6 h. These trends suggest the possibility of full PBI transformation into PBA by simply adjusting the reaction time when operating at 160 °C.

Table 1

Textural and physical characteristics properties of the different Pd-supported catalysts (2.3 wt.%) prepared in this study and performance in the alkylation reaction of aniline with benzyl alcohol. *Reaction conditions*: 1 A : 3 BA, 60 mg catalyst, 160 °C, 3 h, 600 rpm, 1 bar N₂.

Samples	BET surface area (m ² /g)	Acid-base nature	Pd doping	Max. Pd size (nm)	Aniline conversion (%)	Yield (%)			
						PBI	PBA	DBA	Others
Pd/K-OMS-2	96	Acid/basic (+)	Ion exchange	NP	99	3	96	-	-
Pd/H-K-OMS-2	84	Acid (+)		NP	56	23	33	-	-
Pd/MnO ₂ (amorph.)	94	Acid (+)		NP	64	25	39	-	-
Pd/Mn_2O_3	11	Basic (+)		NP	76	26	50	-	-
Pd/SiO ₂	200	Acid (+)	IWI ^b	<5	42	13	27	1	1
Pd/TiO ₂	150	Acid (+)		-	73	41	34	-	-
Pd/Al ₂ O ₃	200	Amphoteric		-	87	26	61	-	-
Pd/Fe ₂ O ₃	60	Basic (+)		10-50	100	24	74	2	-
Pd/C ^a	>1000	Neutral		5	60	24	35	-	1
$Pd/Fe_2O_3^{c}[37]$	60	Basic (+)	Co-precip.	3	99	3	96	0	0
Pd/MgO ^d [38]	670	Basic (++)	IWI‡	<5	96	12	80	0	0

^a 5 wt.% Pd.

^b Incipient wetness impregnation.

^c Prepared by co-precipitation at RT.

^d Prepared by IWI (0.8 wt% Pd); reactions conditions: benzyl alcohol (1 mmol), aniline (3 mmol), *n*-dodecane (0.1 mmol), Pd (0.0075 mmol), trifluorotoluene (1 mL), $T = 180 \degree$ C, time = 6 h.



Fig. 3. Influence of the reaction time on the catalytic activity and selectivity for the Pd/K-OMS-2 catalyst in the alkylation reaction of aniline with benzyl alcohol under inert atmosphere. *Reaction conditions*: 1 A:3 BA, 60 mg catalyst, 160 °C, 600 rpm, 1 bar N₂ atmosphere.

At lower temperatures (i.e., 120 and 140 °C, results not shown), a maximum PBI yield about 85% could only be reached after 3 h reaction time. In all cases, irrespective of the reaction time and temperature, neither the tertiary amine (DBA) nor other reduced by-products such as toluene were detected even after 6 h of reaction.

3.2.2. Influence of the catalyst weight

To survey the effect of the catalyst weight on the performance of the Pd/K-OMS-2 catalyst, a series of devoted catalytic tests were carried out at standard reaction conditions, with the catalyst weight varied in the range 7.5–90 mg (Fig. 4). Within the limits of the experimental error, the aniline conversion and PBA yield were kept at high values and essentially unchanged with the catalyst weight in the range 30–60 mg. At lower weights (i.e., 7.5 and 15 mg), the conversion declined with a relative increase in the PBI yield, whereas at 90 mg, the aniline conversion increased at the expense of a decline in the PBA selectivity.



Fig. 4. Influence of the catalyst weight effect on the activity and selectivity of the Pd/K-OMS-2 catalyst in the alkylation reaction of aniline with benzyl alcohol under N_2 atmosphere. Other reaction conditions as in Fig. 3.

3.2.3. Influence of the atmosphere

The nature of the atmosphere in direct contact with the reaction mixture was found to affect the selectivity of our Pd/K-OMS-2 catalyst (Fig. 5). As a matter of fact, when air was used instead of N₂ at the very same reaction conditions, the PBA selectivity decreased to 56% from a value of 93%. In both cases, almost full aniline conversion was reached. The severe impact of the atmosphere on the catalyst selectivity can be explained by the relative competition between molecular oxygen and PBI as electron acceptors, mitigating the capacity of the catalyst to borrow stored "H₂" in the absence of strictly inert conditions.

3.2.4. Activity and selectivity in successive runs

The reusability of the Pd/K-OMS-2 catalyst was tested in three consecutive runs in the alkylation reaction of aniline with benzyl alcohol. After each run, the catalyst was recovered, washed with a 50:50 water acetone solution, and dried at 120 °C before use for the next run. After the first run, the catalyst kept a selectivity >90% to PBA with an aniline conversion about 70%. We attribute this hampered activity after the first run to a phase conversion of the original Pd/K-OMS-2 catalyst. For the sake of clarity, this new phase will be termed as Pd/MMO (MMO for "modified manganese oxide") in the remainder of this study.

3.3. Structure-activity relationship in Pd/K-OMS-2

3.3.1. PXRD patterns

Fig. 6 plots the XRD patterns of the regular K-OMS-2, the Pd/K-OMS-2, and the Pd/MMO phase after reaction. For both the K-OMS-2 and Pd/K-OMS-2 samples, the XRD patterns showed characteristic (110), (200), (220), (310), (211), (301), (411), (600), (521), (002), (541), (312), (402), and (332) reflections belonging, respectively, to 2-theta angles 12.7°, 18.0°, 22.0°, 28.7°, 37.4°, 42.0°, 49.8°, 56.1°, 60°, 65.3°, 69.3°, 73.1°, 77.5°, and 78.7° which can be attributed to the synthetic cryptomelane (KMn₈O₁₆, JCPDS No: 42-1348, *I4/m* tetragonal unit cell) with no indication of other phase impurities attributed to manganese oxides. Furthermore, in the case of the Pd/K-OMS-2, no reflections indicative of palladium oxide formation were observed (the more intense peak of PdO should appear at about 2-theta = 33.5°), suggesting a high dispersion of Pd on K-OMS-2 or substitution into the framework. The average crystallite size calculated by applying Scherrer equation



Fig. 5. Influence of the reaction atmosphere on the catalytic activity and selectivity of the Pd/K-OMS-2 catalyst in the alkylation reaction of aniline with benzyl alcohol. Other reaction conditions are shown in Fig. 3.



Fig. 6. XRD patterns of (a) K-OMS-2, (b) Pd/K-OMS-2, and (c) Pd/MMO after the amination reaction.

to the strongest reflection (2-theta = 37.4°) was 23 nm for both K-OMS-2 and Pd/K-OMS-2.

After one reaction run, the original Pd/K-OMS-2 phase was converted into a pure hausmannite phase showing a spinel structure (hausmannite = Mn_3O_4 , JCPDS No: 24-0734) with characteristic reflections at 2-theta = 18, 31.4, 32.5, 36.1, 38.3, 44.5, 51, 54.1, 56.1, and 64.7. An additional peak at about 19° was observed corresponding probably to the MnO_2 phase. No peaks corresponding to metallic Pd, PdO or PdO₂ or K₂O/KOH were observed, suggesting a good dispersion or partial incorporation of Pd and K onto/into the hausmannite phase. The estimated crystallite size using Scherrer equation applied to the peak centered at 2-theta = 37.4 was about 23 nm, matching the sizes estimated on the parent K-OMS-2 and the fresh Pd/K-OMS-2 samples, suggesting no modification of the crystallite size after the amination reaction.

3.3.2. TEM/HRTEM

The morphology of the fresh Pd/K-OMS-2 and used Pd/MMO catalysts was inspected by TEM and HRTEM (Figs. 7 and 8). Both samples kept a needle-like morphology of the raw K-OMS-2 (ESI, Fig. S2), showing fibers with 50–250 nm length and 5–20 nm width matching the dimensions obtained on the parent K-OMS-2 sample. Transposing these dimensions into an equivalent spherical size, the maximum crystallite size can be estimated at about 20 nm for both K-OMS-2 and Pd/K-OMS-2, matching the values obtained by direct application of Scherrer equation to the (211) reflection (23 nm).

A deeper inspection of the microstructure of the Pd/K-OMS-2 sample using HRTEM (Fig. 7B) showed the presence of lattice fringes separated by a distance of 0.48 nm. This distance matches the (200) d-spacing of the K-OMS-2 phase (reflection appearing at 2-theta = 18.0, Fig. 6) [68], confirming the formation of a cryptomelane phase with no visible structural modification after Pd incorporation. Although ICP-AES and EDX analyses confirmed the presence of Pd in the sample (ca. 2. wt.%), the TEM and HRTEM micrographs did not evidence supported Pd nanoparticles on K-OMS-2 after ion exchange. This observation, matching the general picture obtained on Pd-exchanged amorphous MnO₂ and Mn₂O₃ (ESI, Fig. S3), suggests Pd incorporation either in the cryptomelane channels by preferential K-substitution, or in the framework via exchange of octahedrally coordinated Mn ions. Both scenarios are compatible with the very similar XRD patterns obtained for the Pd-doped and parent K-OMS-2 samples (Fig. 6), revealing an insignificant change in both the symmetry and unit cell parameters of the cryptomelane phase after Pd incorporation.

3.3.3. Surface area and porosity

Fig. S3 (see ESI) plots the N₂ adsorption/isotherms at 77.4 K for the fresh Pd/K-OMS-2 catalyst and the same sample after reaction (i.e., Pd/MMO). Both samples showed a characteristic Type II sorption pattern matching the general behavior observed for the raw K-OMS-2 (not plotted in Fig. S3 for the sake of clarity) indicative of multilayer adsorption. Furthermore, the isotherms showed the presence of a distinct H3-type hysteresis loop between the adsorption and desorption branches for $P/P_0 > 0.6$ that can be attributed to intercrystalline mesopores between nearby particles with nonuniform size or shapes. The hysteresis loop closed at a higher pressure for the Pd/MMO sample, reflecting a slight increase of intercrystalline pore size during the amination reaction.

The BET-specific surface and total pore volume of the K-OMS-2, Pd/K-OMS-2, and Pd/MMO samples showed in all cases similar values in the range 80–100 m²/g and 0.4–0.5 cm³/g, respectively (Table 2). The BJH pore size estimated from the adsorption curve was about 12 nm for the three samples. The application of the *t*-plot method reflected a major contribution of the external surface area at a level higher than 60% for the former two samples, whereas the BET-specific surface of the Pd/MMO sample corresponded completely to the external surface. Indeed, the measured BET surfaces are in good agreement with the theoretical values that can be deduced from the crystallite size, about 60 m²/g assuming a spherical shape and taking a density of 4.3 g/cm³ for all the samples [69]. The estimated micropore volume for the former two samples was about 0.43 cm³/g, whereas the last sample displayed a negligible value as expected for a non-porous solid.



Fig. 7. TEM micrographs of the fresh Pd/K-OMS-2 sample: (a) low resolution, and (b) high-resolution showing (200) lattice fringes.

 Table 2

 Textural properties, phase, and bulk chemical composition of Pd-modified catalysts.

Catalysts	BET surface area (m²/g)	External surface area (m²/g)	Pore volume (cm ³ /g)	Phases (XRD)	Crystallite size (nm) ^a	H ₂ consumption (TPR-H ₂) (mmol/g)
K-OMS-2	96	82	0.52	Cryptomelane (γ-MnO ₂)	24	11.8
Pd/KOMS-2	93	79	0.35	Cryptomelane (γ-MnO ₂)	24	12.2
Pd-MMO	93	93	0.43	Hausmannite (Mn_3O_4)	23	7.8

^a Computed using Scherrer equation from the more intense reflection in the XRD pattern (2-theta = 37.4°).

The results stated above suggest a major contribution of N₂ adsorption at the external surface of the particles, but with negligible adsorption in the OMS-2 channels in the former two samples. Accordingly, N₂ adsorption at 77.4 K appears to be "invisible" micropores, such behavior being at the origin of the Type II form of the N₂ isotherm instead of the rather expected Type I as in the case of zeolites. Such observation, already reported by Suib and co-workers [70] on a variety of OMS-type frameworks, is attributed to a hindered diffusion of N₂ into the OMS-2 micropores at cryogenic temperatures. As a way out of this shortcoming, CO₂ physisorption at 273 K was claimed to offer a proper measurement of the microporosity of OMS-2 samples due to the improved diffusion of CO₂ into the channels. In our case, we restricted the characterization to N₂ adsorption, since the active sites for amination are expected to be located at the external surface of Pd/K-OMS-2 crystals (vide infra).

3.3.4. IR spectra

The lattice vibrational behavior of the different samples was studied using FTIR spectroscopy to probe the effect of Pd substitution on the spectral features of K-OMS-2 and assess the evolution of the Pd/K-OMS-2 sample after reaction. Fig. 9 plots the different IR spectra obtained. Both K-OMS-2 and Pd/K-OMS-2 showed four characteristic bands around 721, 606, 530, and 471 cm⁻¹ with comparable relative intensities that can be assigned to Mn–O lattice vibration modes in [MnO₆] octahedra [71]. Furthermore, no peak ascribed to adsorbed water in the tunnels was observed (about 1627 cm⁻¹), suggesting a proper outgassing of the samples and low hydration kinetics under ambient atmosphere.

After the reaction, the Pd/MMO sample exhibited two bands centered at 614 and 513 cm⁻¹ that can be attributed, respectively, to Mn–O vibrations in tetrahedral and octahedral environments [72]. The former two bands are compatible with the crystalline data obtained on the XRD patterns, pointing out the presence of two different environments for Mn (tetrahedral and octahedral) as expected for the hausmannite phase (spinel structure). Even after washing, characteristic bands belonging to adsorbed N-phe-nyl benzylamine could be detected (i.e., 1596, 1504, 1452, 1429, 1374, 1065, 1028, 989, 868, 714, and 510 cm⁻¹), but with no



Fig. 9. IR spectra of K-OMS-2, Pd/K-OMS-2, and Pd/MMO.

indication of neither adsorbed benzyl alcohol (in excess during the reaction) nor aniline (fully consumed during the reaction).

3.3.5. H₂-TPR profiles

The H₂-TPR profiles of the raw K-OMS-2, Pd/K-OMS-2 and Pd/ MMO catalysts are presented in Fig. 10, while the corresponding H₂ consumption is listed in Table 2. The raw K-OMS-2 displayed two characteristic peaks appearing in the temperature range 255–300 °C, which are attributed to the two-step reduction of K-OMS-2 to Mn₃O₄ and further Mn₃O₄ to MnO at higher temperature. Although no information regarding the oxidation state of Mn could be unambiguously inferred from the H₂ consumption, the value measured (11.8 mmol/g) is in good agreement with the expected value for complete reduction of MnO₂ to MnO (11.5 mmol/g).

The reduction behavior of K-OMS-2 showed a drastic change after doping with Pd (i.e., Pd/K-OMS-2), the two characteristic peaks being displaced to 45-120 °C, but with a comparable H₂ consumption as for the parent K-OMS-2 (Table 2). This observation is

Fig. 8. TEM micrographs of the Pd/MMO sample after the amination tests: (a) low resolution and (b) high resolution.

Fig. 10. TPR-H₂ profiles of the K-OMS-2, Pd/K-OMS-2, and Pd/MMO.

classically linked to the formation of hydrides over noble metal islands (in our case Pd), transferring fast to the MnO_x phase by spillover and favoring accordingly its reduction [73]. Note, however, that the temperature range for reduction found in this study is remarkably lower than the range reported by Liu et al. [74] on supported PdO/K-OMS-2 (110–190 °C for 2.5 wt.% Pd), most likely due to a better dispersion of Pd in our case. No distinguishable peak attributed to Pd was detected, being most probably included in the main peak appearing at ca. 45 °C. In such situation, the larger H₂ consumption for the Pd/K-OMS-2 sample compared to the value measured for K-OMS-2 (about 3.5%) could be tentatively ascribed to Pd(II) or Pd(IV) moieties either incorporated or supported over K-OMS-2.

After the amination reaction, the Pd/MMO phase showed a markedly different reduction profile compared to the fresh Pd/K-OMS-2 sample. Indeed, a sole reduction peak was observed centered at 180 °C with a H₂ consumption about 7.8 mmol/g, in good agreement with the theoretical value of 8.3 mmol/g for hausmannite (Mn₃O₄ = MnO + Mn₂O₃), involving a distribution of Mn cations as 1/3 Mn(II) and 2/3 Mn(III).

3.3.6. TGA analyses

The thermal stability of the different samples was assessed using TGA/DTG analysis. Fig. 11 plots the different thermal patterns obtained under N₂ atmosphere using a heating ramp of 5 °C/min. The K-OMS-2 and Pd/K-OMS-2 samples showed qualitatively similar thermal patterns characterized by four main steps: (i) 50–200 °C (2 wt.% loss) attributed to physisorbed water, (ii) 350–460 °C (4 wt.% loss) ascribed to chemisorbed O₂ and water, (iii) 490–570 °C (3 wt.% loss) involving the liberation of lattice oxygen from the cryptomelane phase of deoxygenation of MnO₂ to Mn₂O₃, and (iv) 630–730 °C (2 wt.%) due to the conversion of Mn₂O₃ into Mn₃O₄ (hausmannite). However, the K-OMS-2 framework showed a higher thermal stability after Pd incorporation with no additional weight loss steps.

A different thermal pattern was observed for the Pd/MMO sample after reaction. The TGA/DTG profiles were obtained after washing the sample to remove the adsorbed organic compounds. As a matter of fact, this sample showed three main weight loss steps: (i) 50–200 °C (2 wt.% loss) attributed to adsorbed water and some remaining organic products according to the evolution of the H₂O and CO₂ concentration in the gas stream (Fig. S4) and to the FTIR spectra (Fig. 9), (ii) 250–430 °C (14.3 wt.% loss) due to elimination of organic products, and (iii) 520–650 °C (1.2 wt.% loss) due to removal of residual organic fragments.

Fig. 11. TGA/DTG thermal profiles for the K-OMS-2, Pd/K-OMS-2 and Pd/MMO samples (upper and middle plots), and evolution of the O_2 concentration in the gas stream (lower plot). Additional plots on the evolution of the CO_2 , H_2O and NO concentration in the gas stream can be found in the ESI.

3.3.7. Elemental analyses

Table 3 lists the bulk Mn, K, and Pd composition (weight basis), as well as the average oxidation state (AOS) of the different samples prepared in this study as inferred from EDX elemental analysis. First, Pd incorporation to the K-OMS-2 framework triggered a decrease in the manganese composition from 94.3 wt.% to 91.1 wt.%, whereas K only decreased about 12% to afford the

able 3	
ulk Mn, K, and Pd composition measured by EDX in the K-OMS-2, Pd/K-OMS-2 and Pd/MMO samples.	

Catalysts Molar fraction (%)			Weight f	fraction (wt.%)	Molar ratio	Molar ratios (R, –)			
	Mn	К	Pd	Mn	К	Pd	K/Mn	Pd/Mn	Pd/K	
K-OMS-2	92.2	7.83	-	94.3	5.70	-	0.0849	_	_	3.96
Pd/K-OMS-2	91.0	7.03	1.97	91.1	5.02	3.82 (2.3 wt.%) ^b	0.0774	0.0216	0.28	3.97
Pd/MMO	95.6	2.77	1.68	94.8	1.96	3.23	0.0290	0.0176	0.606	-

^a Values measured from the K/Mn and K/Pd molar ratios in K-OMS-2 and Pd/K-OMS-2 samples.

^b Value measured by ICP-AES.

molecular formula $K_{0.63}Mn_{7.83}Pd_{0.17}O_{16}$. As a result, the K/Mn molar ratios showed a modest decrease from 0.0849 in K-OMS-2 to 0.0774 in Pd/K-OMS-2. Taking into account the large amount of Pd incorporated into the K-OMS-2 sample (3.82 wt.% in Mn, K, and Pd basis) overcoming largely the K removal (0.70 wt.% in the same basis), we might attribute the decline in the K composition to a slight yet measurable increased oxidation state of the sample. Assuming that no Pd occupied VIII-coordinated channel sites (see justification below), the AOS of both samples was estimated using the following expression obtained by imposing the condition of charge balance in the OMS-2 framework

$$AOS = 4 - R_{K/(Mn+Pd)}$$
(1)

where $R_{K/(Mn+Pd)}$ is the K/(Mn + Pd) molar ratio showing limiting values between 0 (AOS = 4) and 1 (AOS = 3). This ratio can be computed from the experimental K/Mn and K/Pd ratios listed in Table 3 using the expression

$$\frac{1}{R_{K/(Mn+Pd)}} = \frac{1}{R_{K/Mn}} + \frac{1}{R_{K/Pd}}$$
(2)

In the presence of Pd, Eq. (1) applies only if Pd replaces octahedral Mn sites in OMS-2 either as Pd(II) or Pd(IV), but with no clear

distinction about the oxidation state of Pd due to the potential subtle interplay between substituted Pd cations and Mn(III)/Mn(IV) species. In contrast, in the absence of Pd or if this is dispersed over the external surface of K-OMS-2, $R_{K/(Mn+Pd)}$ transforms into $R_{K/Mn}$. More details on this point supporting also our choice for Eq. (1) for inferring the AOS of the Pd/K-OMS-2 sample is provided below.

After the reaction, the Pd/MMO phase showed a markedly higher Mn bulk concentration (ca. 95 wt.%), but with a strong decrease in the K concentration from the initial value of 5.02 wt.% in the Pd/K-OMS-2 phase to 1.96 wt.% in Pd/MMO most probably due to partial leaching. In contrast, the Pd concentration kept essentially unchanged.

3.3.8. XPS

A complete XPS study was conducted to gain insight into the oxidation state, surface composition, and atomic environment of Mn, K, and Pd species in the different samples under study. Figs. 12 and 13 show, respectively, the experimental and simulated spectra obtained for the corresponding Mn3s/Mn2p/Pd3d and K2p/O1s core levels, while Tables 4 and 5 compile, respectively, the binding energies (BE) and surface composition of the Mn, K and Pd species after peak deconvolution. Detailed spectra for the range 0–1200 eV

Fig. 12. XPS spectra of (a-c) Mn3s, (d-f) Mn2p, (g and h) Pd3d, (i-k) O1s, and (i-n) K2p core levels for K-OMS-2, Pd/K-OMS-2, and Pd/MMO.

Fig. 13. XPS spectra of the O1s core levels for (a) K-OMS-2, (b) Pd/K-OMS-2, and (c) Pd/MMO.

Table 4 Mn, K, and Pd binding energies (main peak values, eV), spin-orbit energies (eV), and relative peak intensities (-) in the K-OMS-2, Pd/K-OMS-2, and Pd/MMO samples.

Catalyst	Mn3s			Mn2p			К2р			Pd3d		
	BE Mn3s(1)	BE Mn3s(2)	∆BE Mn3s	BE Mn2p _{1/2}	BE Mn2p _{3/2}	∆BE Mn2p	BE K2p _{1/2}	BE K2p _{3/2}	∆К2р	BE Pd3p _{3/2}	BE Pd3p _{5/2}	∆Pd3d
K-OMS-2 Pd/K-OMS-2 Pd/MMO	88.7 88.6 88.6	84.0 84.0 83.0	4.7 4.6 5.6	653.9 654.1 653.7	641.9 641.8 641.0	12.0 12.3 12.7	294.0 293.8 295.0	291.0 290.8 292.0	3.0 3.0 3.0	- 342.6 342.9/340.9	- 337.2 337.8/335.7	- 5.4 5.1/5.2

Table 5

Surface composition measured from XPS and relative abundance of the different oxidation states in the K-OMS-2, Pd/K-OMS-2, and Pd/MMO samples.

Catalyst	Molar f	Molar fraction (%)			Molar ratio (R, –)			Mn species (%)			Pd species (%)	
	Mn	K	Pd	K/Mn	Pd/Mn	Pd/K	Mn(IV)	Mn(III)	Mn(II)	Pd(Ox)	Pd(Red)	
K-OMS-2	91.3	8.66	-	0.0948	-	-	100	ND	0	-	-	3.97
Pd/K-OMS-2	89.2	8.70	2.12	0.0976	0.0239	0.245	100	ND	0	100	0	3.96
Pd/MMO	89.1	9.74	1.20	0.109	0.0133	0.122	0	67	33	50	50	2.70

^a Values measured from the K/Mn and Pd/Mn molar ratios in K-OMS-2 and Pd/K-OMS-2 samples and from the relative surfaces of Mn(III) and Mn(II) moieties in Mn2p peaks in the Pd/MMO sample (Figs. 12 and 13).

can be found in the ESI (Fig. S5). For all the samples, the Mn3s (Fig. 12A–C) and Mn2p (Fig. 12D–F) core levels were split into two peaks (Mn3s(1)/Mn3s(2) and Mn2p_{3/2}/Mn2p_{5/2}, respectively) due to symmetric/antisymmetric spin correlations between the

Mn2p and Mn3s unpaired electrons and the $5d^{N}$ electrons (i.e., t_{2g} and e_{g} for O_{h} symmetry in high-spin configuration) in the valence shell of Mn (N = 3, 4, and 5 for Mn(IV), Mn(III), and Mn(II), respectively). An additional smaller peak appeared at higher BE

that can attributed to a shake-up satellite for the $Mn2p_{1/2}$ level encompassing a concomitant 2-electron transfer [75].

Only Mn(IV) could be unambiguously discriminated in both the K-OMS-2 and Pd/K-OMS-2 samples, as inferred from the characteristic BEs of the Mn3s and Mn2p doublets, at about 88.6/84.0 eV and 650/641.8 eV (Fig. 12D and E), respectively, with a relative intensity of 1.8:1 and 1.4:1. However, this fact does not exclude the presence of a small and hardly detectable amount of Mn(III) cations in the cryptomelane framework. The spin-orbit splitting or energy difference between the $Mn2p_{1/2}$ and $Mn2p_{3/2}$ levels was slightly shifted from 12.0 to 12.3 eV after Pd incorporation, whereas the spin-orbit energy for the Mn3s level was kept essentially unchanged at a value of 4.6-4.7 eV, suggesting either the absence or lack of detectable variation in the AOS of Mn after Pd incorporation [76]. The surface Mn composition in the cryptomelane framework evolved from an initial value of 93.7 wt.% in K-OMS-2 to 89.6 wt.% in Pd/K-OMS-2 with a change in the K/Mn molar ratios from 0.0948 to 0.0979, respectively, suggesting partial Mn substitution by Pd. This reduction is similar to that measured for the bulk Mn composition, reflecting a reasonable homogeneity of the Pd distribution within the particle thickness.

After the amination reaction, the Pd/MMO phase exhibited a moderate decrease in the Mn2p and Mn3s BEs with values of 88.6/83.0 eV (Fig. 12C) and of 653.7/641.0 eV (Fig. 12F), respectively, for the corresponding doublets, whereas the spin–orbit energies decreased in each case to values of 5.7 and 12.7 eV. The relative intensity of Mn3s(1)/Mn3s(2) and Mn2p_{3/2}/Mn2p_{1/2} peaks kept unmodified at 1.8:1 and 1.5:1, respectively. These observations are consistent with a reduction in the AOS of the Pd/MMO phase after reaction (Table 5). The XPS patterns for each level could be successfully deconvoluted into two primary bands attributed to Mn(III) and Mn(II) cations with the relative intensity 2:1 matching the expected stoichiometry of hausmannite.

The Pd3d spectrum of Pd/K-OMS-2 sample (Fig. 12G) also showed a characteristic doublet that can be assigned to the Pd3d_{3/2} and Pd3d_{5/2} core levels. The corresponding BEs showed unexpectedly high values, about 342.6 and 337.2 eV (Table 4), respectively, with a spin-orbit energy of 5.4 eV and relative intensity of 1:1.7 between the peaks. After the reaction, the Pd3d spectrum of the as-generated Pd/MMO phase showed the presence of two additional bands appearing at lower energies (i.e., 340.9 and 335.7 eV, Fig. 12H). This result suggests the formation of reduced Pd species after reaction. The relative intensity between the oxidized and reduced Pd species was 1:1. The bulk Pd composition was only slightly reduced after the synthesis, confirming a lack of leaching from the support. In contrast, the surface Pd composition measured by XPS showed a remarkable decrease after the reaction. Such observation seems to indicate a segregation of Pd within the particle thickness in Pd/MMO, involving also a possible segregation of oxidation states.

The K2p spectra of the different samples (Fig. 13L-N) also comprised two peak components with no observable satellites. The corresponding BEs for the different peaks increased after reaction from the values of ca. 294 and 291 eV ($K2p_{3/2}$ and $K2p_{1/2}$) in both K-OMS-2 and Pd/K-OMS-2 to 295.0 and 292.0 eV ($K2p_{3/2}$ and K2p_{1/2}) after reaction (i.e., Pd/MMO). However, the corresponding spin-orbit energies remained unchanged at a value of 3.0 eV with an intensity ratio between the $K2p_{3/2}/K2p_{1/2}$ peaks at 2:1. This body of data supports a dramatic change in the K environment after the reaction, evolving from a highly dispersed eight-coordinated environment inside the cryptomelane tunnels into a surface-segregated K₂O or KOH phase in hausmannite (the K2p BEs in K₂O are about 295.7 and 292.9 eV [77]). This hypothesis can be reinforced by the difference in the bulk and surface K compositions in Pd/MMO (Table 5). As a matter of fact, the bulk K composition decreased from an initial value of 5.02 wt.% in Pd/K-OMS-2

Table 6

Binding energy and relative abundance of the different oxygen species in K-OMS-2, Pd/K-OMS-2, and Pd/MMO samples.

Catalyst	01s (O _I)		01s (O _{II})			
	BE (eV)	Abundance (%)	BE (eV)	Abundance (%)		
K-OMS-2 Pd/K-OMS-2 Pd/MMO	531.5 530.9 530.8	34 28 72	529.5 529.5 529.5	66 72 28		

to 1.96 wt.% in Pd/MMO after reaction, suggesting partial removal, whereas the surface K composition exhibited the opposite trend, increasing from 6.22 to 7.05 wt.%.

Finally, it is worth noting an outstanding change between the O1s patterns for K-OMS-2 and Pd/K-OMS-2 and that of Pd/MMO. Fig. 13I–K plots the corresponding spectra. In all cases, the O1s spectrum clearly showed two characteristic bands after deconvolution that are classically attributed to framework O^{2-} species (O_{II}) and surface O^{2-} , O^- , and OH species and oxygen vacancies (O_I). An additional band corresponding to adsorbed H₂O could be also deconvoluted for K-OMS-2, but with a very modest surface (<2%). The O_{II} BE was kept unchanged for all the samples at a value of 529.5 eV, whereas the O_I BE decreased noticeably after Pd incorporation (from 531.5 to 530.9 eV) and kept a similar value after reaction.

The relative intensity of O_{II} and O_{I} species (Table 6) was also affected by the introduction of Pd into the K-OMS-2 framework, showing a decline of O_{I} moieties (34% in K-OMS-2 vs. 28% in Pd/K-OMS-2). In contrast, after reaction, the Pd/MMO sample became enriched in O_{I} moieties (28% in Pd/K-OMS-2 vs. 56% in Pd/MMO). These results point out an outstanding increase in surface defects after the reaction, this factor being most likely linked to the promoted activity and selectivity of the Pd/K-OMS-2 for amination. The impact of such defects on the catalytic activity is discussed below.

4. Discussion

4.1. Location and oxidation state of Pd centers in Pd/K-OMS-2

The body of data collected in the Results section provides clear evidence of a very good Pd dispersion over K-OMS-2 in the Pd/K-OMS-2 sample before reaction and also in the as-generated Pd/MMO hausmannite phase after reaction with no observable formation of supported palladium oxide nanoparticles. Pd can be localized a priori in three possible environments: (1) inside the K-OMS-2 channels as Pd(II), encompassing partial substitution of the original K⁺, (2) in the K-OMS-2 framework as Pd(II) or Pd(IV) via a partial substitution of octahedral Mn(IV) or Mn(III), and (3) finely dispersed over or embedded into K-OMS-2 as PdO_x nanoparticles. The former option appears to be excluded in light of the bulk and surface Pd and K composition in Pd/K-OMS-2. Indeed, even if the bulk K loading decreased after Pd loading compared to the initial value in K-OMS-2, this reduction was much lower than the loaded Pd (compare the values of 7.83-7.03 = 0.80 mol% for K change with 1.97 mol% for Pd loading in Mn, K and Pd basis, Table 3). Moreover, the surface K concentration kept unchanged after Pd incorporation (Table 5), confirming the lack of significant K-substitution by Pd even at sublayers near the external surface of K-OMS-2.

The third option also seems discouraged, since no evidence of the formation of PdO_x nanoparticles was found in the HRTEM micrographs for neither Pd/K-OMS-2 (Fig. 7) nor Pd/MnO₂ and Pd/Mn₂O₃ (Fig. S2). Moreover, as stated above, the similar bulk and surface Pd concentrations suggest a homogeneous distribution

of Pd within the K-OMS-2 particle thickness, suggesting no embedding of PdO_x nanoparticles by cryptomelane. The first observation opposes to the results reported by Liu et al. [74], where supported PdO nanoparticles on K-OMS-2 could be unambiguously identified by the presence of a characteristic reflection at 2-theta = 30° in the XRD patterns for samples with Pd loading ≥ 2.5 wt.%. Moreover, the H₂-TPR tests performed on those samples at comparable experimental conditions and for similar particle sizes reflected much higher reduction temperatures than our Pd/K-OMS-2 sample (Fig. 10), suggesting in their case a less efficient formation of hydrides.

According to the above-stated reasons, only the second option, namely Pd substitution into the cryptomelane framework, appears to be feasible. The fact that the bulk and surface Mn concentrations decreased after Pd incorporation in a similar degree as loaded Pd (Table 3) provides a direct evidence of such hypothesis. Partial Pd substitution into the cryptomelane framework encompasses a slight yet detectable increase in the AOS of Mn from 3.95 in the parent K-OMS-2 to 3.97 in Pd/K-OMS-2. This increase might be at the origin of the observed reduction in the bulk K concentration after Pd deposition (compare the bulk K/Mn molar ratio of 0.0849 in K-OMS-2 with the value of 0.0774 in Pd/K-OMS-2). The high AOS approaching 4 might explain why only Mn(IV) could be unequivo-cally distinguished in the XPS spectra for both Mn3s and Mn2p core levels (Fig. 12A, B, D and E).

Based on this rationale, the next point to elucidate is the oxidation and local environment of Pd. This question is crucial to further unveil the nature of the active sites for amination. The existence of a high-valent Pd species, most likely Pd(IV), in place of Mn in the cryptomelane framework appears to be a priori the best option due to symmetry reasons (Pd(II) prefers planar IV-fold environments, whereas Pd(IV) can accept octahedral coordination), and to the similar ionic radii of Pd(IV) and Mn(IV)/Mn(III) under a VIII-fold environment (6.2 Å for Pd(IV) vs. 5.3 Å for Mn(IV) and 5.8 Å for Mn(III) compared to 8.6 Å for Pd(II) [78]). This hypothesis is supported by the abnormally high Pd3d_{5/2} BE measured on Pd/K-OMS-2 (337.2 eV, Table 4), becoming even larger after reaction (i.e., 337.8 eV), compared to the values that would be expected for standard PdO and Pd(0). As a general rule, the $Pd3d_{5/2}$ BEs show values in the range 335.2-337.1 eV for PdO, and 334.1-336.4 for Pd(0) [79,80], increasing inversely with the nanoparticle size [81]. The Pd3d_{5/2} BE measured in our study is also slightly larger than the values reported on Pd/MnO_x [82], Pd/MnCeO_x [83], and Pd/K-OMS-2 [74] (up to 337.1 eV) based on highly dispersed supported PdO nanoparticles (<4.5 nm), appearing within the common range for bulk and dispersed PdO₂ (337.6–338.6 eV [37,84,85]).

Assuming that Pd(IV) was the dominant species and imposing charge balance in the cryptomelane framework, the following two-cation exchange (redox) processes can be proposed accounting for Mn substitution by Pd

$$Pd_{(aq)}^{2+} + {}^{VI}Mn(IV) \rightarrow {}^{VI}Pd(IV) + Mn_{(aq)}^{2+}$$

$$(3)$$

$$\begin{split} ^{\text{VI}}\text{Mn}(\text{III}) + \text{HO}_{\text{OMS}}^{-} + {}^{\text{VIII}}\text{K}^{+} \rightarrow {}^{\text{VI}}\text{Mn}(\text{IV}) + \text{O}_{\text{OMS}}^{2-} + \frac{1}{2}\text{H}_{2} \\ \uparrow + {}^{\text{VIII}}\Theta + \text{K}_{(\text{aq})}^{+} \end{split}$$

where $^{VIII}\Theta^{\circ}$ represent vacant VIII-fold tunnel octahedral sites.

On the one hand, Eq. (3) involves the direct substitution of Mn(IV) by Pd(IV) with no change in the K⁺ distribution within the cryptomelane channel. This process is expected to be favored given the positive standard potential of the process under neutral conditions: $\Delta E \approx E(MnO_2/Mn_{(aq)}^{2+}) - E(PdO_2/PdO) = 1.23 V - 0.73 V = 0.50 V$ [78,86]. On the other hand, Eq. (3) provides a basis for choice of Eq. (1) for inferring the AOS of the Pd/K-OMS-2 sample. Furthermore, Eq. (4) supports the observed enhancement of the

AOS of the cryptomelane framework after Pd substitution, involving in turn a decrease in the K composition and a reduction of O_I oxygen species (Table 6, entries 1 and 2).

According to Eqs. (3) and (4), the molecular formula for Pd/K-OMS-2 proposed in the Results subsection 3.3.7 (*vide supra*) can be resolved to the final form $K_{0.63}Mn(III)_{0.63}Mn(IV)_{7,20}Pd_{0.17}(IV)O_{16}$.

4.2. Reaction scheme: interplay of Pd and K centers

After elucidating the nature of Pd in the cryptomelane framework, we need to address the interplay of Pd and basic centers on the catalytic activity of Pd/K-OMS-2 for amination reactions. The XRD (Fig. 6), FTIR (Fig. 9), and TPR-H₂ (Fig. 10) patterns provide clear evidence of the conversion of the initial Pd/K-OMS-2 into a reduced hausmannite phase (Pd/MMO) after the amination reaction, keeping still high selectivity to the secondary amine (i.e., PBA). The formation of this phase can be described by the following set of redox reactions in the presence of benzyl alcohol as reducing agent

$${}^{VI}Mn(IV) + O_{OMS}^{2-} + \frac{1}{2}C_7H_7OH \rightarrow {}^{VI}Mn(III) + HO_{OMS}^- + \frac{1}{2}C_7H_6O$$
(5)

$$^{VI}Mn(IV) + O_{OMS}^{2-} + C_7H_7OH \rightarrow {}^{IV}Mn(II) + H_2O + C_7H_6O$$
 (6)

$${}^{VI}Mn(III) + O_{OMS}^{2-} + \frac{1}{2}C_7H_7OH \rightarrow {}^{IV}Mn(II) + HO_{OMS}^- + \frac{1}{2}C_7H_6O \qquad (7)$$

The genesis of the hausmannite phase keeps and probably even intensifies the dispersion of Pd(IV) centers in light of the slight but detectable increase in the BEs for $Pd3d_{5/2}$ and $Pd3d_{3/2}$ core levels (342.9 and 337.8 eV, Table 4), generating about 50% of reduced Pd centers most likely based Pd(II) species, as inferred from the new bands appearing at lower BEs in the XPS spectra plotted in Fig. 12H (Pd3d_{5/2} BE = 340.9 eV, Pd3d_{3/2} BE = 335.7 eV, Table 4). The formation of Pd(II) species can be described by the reaction

$$^{VI}Pd(IV) + 2O_{OMS}^{2-} + \frac{1}{2}C_7H_7OH \rightarrow {}^{IV}Pd(II) + 2HO_{OMS}^- + \frac{1}{2}C_7H_6O$$
 (8)

Given the high dispersion of Pd after reaction, we can anticipate that Pd(IV) and Pd(II) species share, respectively, octahedral and tetrahedral sites together with Mn(III) and Mn(II) cations in the spinel structure of hausmannite at a ratio 1:1 (Table 5) to give the molecular formula $Mn(II)_{0.98}Pd(II)_{0.026}Mn(III)_{1.96}Pd(IV)_{0.026}O_{4-}$ 0.085K₂O. These centers might provide optimal interaction with K being expelled from the cryptomelane tunnels during the amination reaction, favoring hydrogen borrowing. In the end, part of the original K in Pd/K-OMS-2 is expected to segregate as surface K₂O or KOH moieties near surface OH groups generated from lattice oxygen (O_{II}) (Table 6, entries 1 and 3), as deduced from the values of the K2p_{3/2} and K2p_{1/2} BEs (295.0 and 292.0 eV, Table 4). The facile release of OH groups is confirmed by the TGA/DTG patterns on Pd/ K-OMS-2 plotted in Fig. 11, favoring the adsorption of benzyl alcohol and therefore the first dehydrogenation step of the hydrogen borrowing mechanism.

In light of the above-stated comments, a tentative scheme of the amination process during the conversion of Pd/K-OMS-2 into Pd/MMO is represented in Fig. 14. Highly dispersed Pd(IV) and Pd(II) species might promote hydrogen borrowing via the generation of stable intermediates, probably involving HO-Pd(IV)-(H)₂ and HO-Pd(II)-H hydride species due to the low energy of formation of the latter species from Pd(II)O hydration in step III (about 7.8 kcal/mol, DFT [37]). This process would be performed near K-OH moieties, favoring the adsorption of benzyl alcohol.

Fig. 14. Hydrogen borrowing mechanism for amine alkylation with alcohols with concomitant Pd/K-OMS-2 conversion into Pd/hausmannite.

5. Conclusions

We have shown along this paper the promising potentials of Pd/ cryptomelane formulations for performing amination reactions operating via the borrowing hydrogen mechanism. A proof of concept was demonstrated for the model alkylation reaction of aniline with benzyl alcohol, affording a PBA yield as high as 96% at 160 °C during 3 h with no formation of neither the tertiary amine nor toluene. The improved performance of this formulation was attributed to a highly active intermediate phase during the reaction including highly dispersed Pd(IV)/Pd(II) species near K and defective OH moieties, favoring hydrogen transfer. After the reaction, the original cryptomelane phase evolved into a Pd/hausmannite phase still showing a high selectivity to PBA (>90%). This study confirms the necessary correlation between surface basicity and hydrogen transfer to perform amination reactions.

A perspective of this study encompasses *operando* studies on the Pd/K-OMS-2 phase under reaction conditions to ascertain the nature of the intermediate species formed during conversion into hausmannite. These studies will be communicated in due time.

Acknowledgments

This study was funded by Solvay and CNRS. The authors would like to express their gratitude to Prof. Feng Shi from the Lanzhou Institute of Chemical Physics (CAS) for insightful discussions on Pd-catalyzed amination mechanisms. The authors are also grateful to Dr. A. Beaurain at UCCS Lille for carrying out the XPS measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.10.003.

References

- H.A. Wittcoff, B.G. Reuben, J.S. Plotkin, Industrial Organic Chemicals, second ed., Wiley, NY, 2004.
- [2] V.A. Veefkind, J.A. Lercher, J. Catal. 180 (1998) 258-269.
- [3] K.S. Hayes, Appl. Catal. A: Gen. 221 (2001) 187–195.
- [4] A.A.N. Magro, G.R. Eastham, D.J. Cole-Hamilton, Chem. Commun. (2007) 3154– 3156.
- [5] G.E. Dobereiner, R.H. Crabtree, Chem. Rev. 110 (2010) 681-703.
- [6] G. Guillena, D.J. Ramon, M. Yus, Chem. Rev. 110 (2010) 1611-1641.
- [7] J.L. Klinkenberg, J.F. Hartwig, Angew. Chem. Int. Ed. 50 (2011) 86–95.
- [8] Fluzard, Bo, Huzard, Internal Rhodia, Report No. 2174, 1954.
- [9] G. Bo, Ph. Perras, Internal Rhodia, Report No. 2932, 1958.
- [10] D.A. Gardner, R.T. Clark, US Patent 4,255,357 to Pennwalt Corporation, 1981.
- J.V. Martinez de Pinillos, R.L. Fowlkes, US Patent 4,314,084 to Air Products and Chemicals Inc., 1982.
- [12] T.L. Renken, H.P. Klein, WO Patent 2009/114438 (A2) to Huntsman Petrochemical Corporation.
- [13] A.K. Rausch, E. van Steen, F. Roessner, J. Catal. 253 (2008) 111-118.
- [14] G.A. Vedage, L.A. Emig, H.-X. Li, J.N. Armor, US Patent 5,917,092 to Air Products and Chemicals Inc., 1998.
- [15] G.A. Vedage, K.S. Hayes, M. Leeaphon, J.N. Armor, US Patent 5,932,769 to Air Products Inc., 1999.
- [16] A. Fischer, T. Mallat, A. Baiker, J. Mol. Catal. A: Chem. 149 (1999) 197–204.
- [17] A. Fischer, T. Mallat, A. Baiker, J. Catal. 182 (1999) 289–291.
- [18] G. Jenzer, T. Mallat, A. Baiker, Catal. Lett. 61 (1999) 111-114.
- [19] M. Imabeppu, K. Kiyoga, S. Okamura, H. Shoho, H. Kimura, Catal. Commun. 10 (2009) 753–757.
- [20] A. Fischer, M. Maciejewski, T. Bürgi, T. Mallat, A. Baiker, J. Catal. 183 (1999) 373–383.
- [21] F. Santoro, R. Psaro, N. Ravasio, F. Zaccheria, ChemCatChem 4 (2012) 1249– 1254.
- [22] K.-I. Shimizu, N. Imaiida, K. Kon, S.M.A. Hakim Siddiki, A. Satsuma, ACS Catal. 3 (2013) 998–1005.
- [23] X. Cui, X. Dai, Y.Q. Deng, F. Shi, Chem. Eur. J. 19 (2013) 3665-3675.
- [24] P.R. Likhar, R. Arundhathi, M.L. Kantam, P.S. Prathima, Eur. J. Org. Chem. (2009)
- 5383–5389. [25] J. Sun, X. Jin, F.W. Zhang, W. Hu, J. Liu, R. Li, Catal. Commun. 24 (2012) 30–33.
- [26] Y. Zhang, S.N. Riduan, Chem. Soc. Rev. 41 (2012) 2083–2094.
- [27] N. Zotova, F.J. Roberts, G.H. Kelsall, A.S. Jessiman, K. Hellgardt, K.K. Hii, Green Chem. 14 (2012) 226–232.
- [28] T. Ichida, H. Kawakita, T. Akita, M. Haruta, Gold Bull. 42 (2009) 267-274.
- [29] Y.S. Demidova, I.L. Simakova, M. Estrada, S. Beloshapkin, E.V. Suslov, D.V. Korchagina, K.P. Volcho, N.F. Salakhutdinov, A.V. Simakov, D.Y. Murzin, Appl. Catal. A: Gen. 464–465 (2013) 348–356.
- [30] X. Cui, Y. Zhang, F. Shi, Y.Q. Deng, Chem. Eur. J. 17 (2011) 1021-1028.
- [31] H. Liu, G.-K. Chuah, S. Jaenicke, J. Catal. 292 (2012) 130–137.

- [32] J.-F. Soulé, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 133 (2011) 18550– 18553.
- [33] K. Uehara, JP Patent 5,148,191 to Idemitsu Petrochemical Co., 1993.
- [34] K. Uehara, JP Patent 6,001,758 to Idemitsu Petrochemical Co., 1994.
- [35] J.W. Kim, K. Yamaguchi, N. Mizuno, J. Catal. 263 (2009) 205–208.
- [36] K. Yamaguchi, J. He, T. Oishi, N. Mizuno, Chem. Eur. J. 16 (2010) 7199–7207.
- [37] Y. Zhang, X. Qi, X. Cui, F. Shi, Y.Q. Deng, Tetrahedron Lett. 52 (2011) 1334– 1338.
- [38] A. Corma, T. Rodenas, M.J. Sabater, Chem. Eur. J. 16 (2010) 254–260.
- [39] S.L. Suib, Acc. Chem. Res. 41 (2008) 479–487.
- [40] J. Cai, J. Liu, W.S. Willis, S.L. Suib, Chem. Mater. 13 (2001) 2413-2422.
- [41] Q. Feng, H. Kanoh, Y. Miyai, K. Ooi, Chem. Mater. 7 (1995) 148–153.
- [42] R. Kumar, S. Sithambaran, S.L. Suib, J. Catal. 262 (2009) 304-313.
- [43] J. Liu, V. Makwana, J. Cai, S.L. Suib, M. Aindow, J. Phys. Chem. B 107 (2003) 9185–9194.
- [44] G.G. Xia, Y.G. Yin, W.S. Willis, J.Y. Wang, S.L. Suib, J. Catal. 185 (1999) 91–105.
 [45] W. Gac, G. Giecko, S. Pasieczna-Patkowska, T. Borowiecki, L. Kepinski, Catal.
- Today 137 (2008) 397-402. [46] X. Yang, J. Han, Z. Du, H. Yuan, F. Jin, Y. Wu, Catal. Commun. 11 (2010) 643–
- 646.
 [47] S. Ching, P.F. Driscoll, K.S. Kielyka, M.R. Marvel, S.L. Suib, Chem. Commun.
- (2001) 2486–2487.
 [48] W.Y. Hernandez, M.A. Centeno, F. Romero-Sarria, S. Ivanova, M. Montes, J.A.
- [46] W.T. Hernandez, M.A. Centerio, F. Koneto-Sarria, S. Ivanova, M. Montes, J.A. Odriozola, Catal. Today 157 (2010) 160–165.
 [49] M. Sun, L. Yu, F. Ye, G. Diao, Q. Yu, Z. Hao, Y. Zheng, L. Yuan, Chem. Eng. J. 220
- (2013) 320–327.
- [50] W.Y. Hernandez, M.A. Centeno, S. Ivanova, P. Eloy, E. Gaigneaux, J.A. Odriozola, Appl. Catal. B: Environ. 123–124 (2012) 27–35.
- [51] H. Nur, F. Hayati, H. Hamdan, Catal. Commun. 8 (2007) 2007-2011.
- [52] L. Sun, Q. Cao, B. Hua, J. Li, J. Hao, G. Jing, X. Tang, Appl. Catal. A: Gen. 393 (2011) 323–330.
- [53] C. Calvert, R. Joersten, K. Ngala, J. Villegas, A. Morey, X. Shen, S.L. Suib, Chem. Mater. 20 (2008) 6382–6388.
- [54] X.-S. Liu, Z.-N. Jin, J.-Q. Lua, X.-X. Wang, M.-F. Luo, Chem. Eng. J. 162 (2010) 151–157.
- [55] H. Tian, J. He, L. Liu, D. Wang, Ceram. Int. 39 (2013) 315-321.
- [56] O. Sanz, J.J. Delgado, P. Navarro, G. Arzamendi, L.M. Gandía, M. Montes, Appl. Catal. B: Environ. 110 (2011) 231–237.
- [57] T. Martínez, L.M. Arzamendi, F. Romero-Sarria, W.Y. Hernández, M.A. Centeno, J.A. Odriozola, Appl. Catal. A: Gen. 423–424 (2012) 137–145.
- [58] Z.-Y. Cai, M.-Q. Zhu, J. Chen, Y.-Y. Shen, J. Zhao, Y. Tang, X.-Z. Chen, Catal. Commun. 12 (2010) 197–201.
- [59] Y.C. Son, V.D. Makwana, A.R. Howell, S.L. Suib, Angew. Chem. Int. Ed. 9 (1999) 319–333.
- [60] F. Schurz, J.M. Bauchert, T. Merker, T. Schleid, H. Hasse, R. Gläser, Appl. Catal. A: Gen. 355 (2009) 42–49.
- [61] V.D. Makwana, Y.C. Son, A.R. Howell, S.L. Suib, J. Catal. 210 (2002) 46–52.

- [62] R. Ghosh, Y.C. Son, V.D. Makwana, S.L. Suib, J. Catal. 224 (2004) 288–296.
- [63] G.D. Yadav, R.K. Mewada, Catal. Today 198 (2012) 330–337.
 [64] H.G. Manyar, B. Yang, H. Daly, H. Moor, S. McMonagle, Y. Tao, G.D. Yadav, A.
- Goguet, P. Hu, C. Hardacre, ChemCatChem 5 (2013) 506–512.
- [65] S. Sithambaram, R. Kumar, Y.C. Son, S.L. Suib, J. Catal. 253 (2008) 269–277.[66] K. Yamaguchi, H. Kobayashi, T. Oishi, N. Mizuno, Angew. Chem. Int. Ed. 51
- (2012) 544–547. [67] G.G. Xia, W. Tong, E.N. Tolentino, N.-G. Duan, S.L. Brock, J.-Y. Wang, S.L. Suib, T.
- Ressler, Chem. Mater. 13 (2001) 1585–1592. [68] N.N. Opembe, C.K. King'ondu, A.E. Espinal, C. Chen, E.K. Nyutu, V.M.
- Crisostomo, S.L. Suib, J. Phys. Chem. C 114 (2010) 14417–14426. [69] S. Dharmarathna, C.K. King'ondu, W. Pedrick, L. Pahalagedara, S.L. Suib, Chem.
- Mater. 24 (2012) 705–712. [70] J. Luo, Q. Zhang, J. Garcia-Martinez, S.L. Suib, J. Am. Chem. Soc. 130 (2008)
- 3198–3207. [71] C.K. King'ondu, N. Opembe, C.-H. Chen, K. Ngala, H. Huang, A. Iyer, H.F. Garcés,
- [71] C.K. King ondu, N. Opennec, C.-n. Chen, K. Ngata, H. Huang, A. Iyer, H.F. Garces S.L. Suib, Adv. Funct. Mater. 21 (2011) 312–323.
- [72] M. Ishii, M. Nakahira, Solid State Commun. 11 (1972) 209–212.
- [73] S.J. Gentry, N.W. Hurst, A. Jones, J. Chem. Soc., Faraday Trans. 1977 (1981) 603– 619.
- [74] X. Liu, J. Lu, W. Wang, M. Luo, Chin. J. Catal. 31 (2010) 181-185.
- [75] M. Oku, K. Hirokawa, S. Ikeda, J. Electron Spectrosc. Relat. Phenom. 7 (1975) 465-473.
- [76] V.R. Galakhov, M. Demeter, S. Bartkowski, M. Neumann, N.A. Ovechkina, E.Z. Kurmaev, N.I. Lobachevskaya, Y.M. Mukovskii, J. Mitchell, D.L. Ederer, Phys. Rev. B 65 (2002) 1131021–1131024.
- [77] B.V. Crist, Handbook of Monochromatic XPS Spectra: The Elements and Native Oxides, vol. 1, John Wiley & Sons, Chichester, 2000.
- [78] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 84th ed., CRC Press, Boca Raton, 2003.
- [79] A.V. Naumkin, A. Kraut-Vass, S.W. Gaarenstroom, C.J. Powell, NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database 20, Version 4.1, http://srdata.nist.gov/xps/selEnergyType.aspx (retrieved 13.06.13).
- [80] M. Peuckert, J. Phys. Chem. 89 (1985) 2481–2486.
- [81] T. Wu, W.E. Kaden, W.A. Kunkel, S.L. Anderson, Surf. Sci. 603 (2009) 2764– 2770.
- [82] H.T. Tan, Y. Chen, C. Zhou, X. Jia, J. Zhu, J. Chen, X. Rui, Q. Yan, Y. Yang, Appl. Catal. B: Environ. 119–120 (2012) 166–174.
- [83] Y. Chen, H. Zheng, Z. Guo, C. Zhou, C. Wang, A. Borgna, Y. Yang, J. Catal. 283 (2011) 34–44.
- [84] D.H. Kim, S.I. Woo, J.M. Lee, O.B. Yang, Catal. Lett. 70 (2000) 35-41.
- [85] L.S. Kibis, A.I. Stadnichenko, S.V. Koscheev, V.I. Zaikovskii, A.I. Boronin, J. Phys.
- Chem. C 116 (2012) 19342–19348.
 [86] A.J. Bard, R. Parsons, R.J. Jordan, Standard Potentials in Aqueous Solutions, IUPAC (Marcel Dekker), NY, 1985.