



The “one-pot” synthesis of 4-methyl-2-pentanone (methyl isobutyl ketone) from acetone over PdCu catalysts prepared from layered double hydroxides

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Abstract

Supported PdCu catalysts prepared from layered double hydroxides (LDHs) as precursors were evaluated in the gas phase reaction of acetone with hydrogen to methyl isobutyl ketone (MIBK). Two series of catalysts containing ca. 0.2 wt.% Pd and various amounts of Cu (Cu/Pd molar ratio of ca. 0.25, 0.5 and 1) were elaborated according to different methods. One series of precursors was obtained by impregnation of calcined Mg(Al)O mixed oxide with heterobinuclear Pd_xCu_{1-x} acetylacetonates. A second series of precursors was synthesized by coprecipitation of Mg/Pd/Cu/Al LDHs. After calcination, both series were reduced at 473 K. The extends of basic, acid and metal functions were evaluated through microcalorimetric adsorption of CO₂, TPD of NH₃ and TPR of H₂. It was found that the multifunctional transformation of acetone to MIBK was rate determined by the basic function. However, the way by which the catalysts were prepared, impregnation or coprecipitation, controls the extend of hydrogenated by-products, isopropyl alcohol and 4-methyl-2-pentanol. The extensive dilution by migrating MgAlO_x species onto the metallic particles makes the coprecipitated catalysts highly selective by decreasing selectively the rate of C=O bond hydrogenation.

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1. Introduction

A contribution to the implementation of greener and sustainable chemistry could be the promotion of catalytic “one-pot” processes. This would allow to reduce the complexity and cost of the separation processes, with, consequently, a reduction of the by-product disposal. A good example is the “one-pot” condensation of carbonyls to higher molecular weight carbonyl

(HMWC) compounds. At present this is performed by an homogeneous conventional three-step process. The latter involves, first a base-catalysed condensation to “aldol”-type intermediate, followed by dehydration of this intermediate on acid sites, and finally the selective hydrogenation of the resulting α,β -unsaturated carbonyl. This process generates huge amounts of wastes. These shortcomings could be avoided by a purely heterogeneous “one-pot” process, and layered double hydroxides (LDH) as precursors of catalysts offer very unique opportunities due to their potential multifunctionality with the combination of basic, acid and metal sites. LDHs may actually be suitable pre-

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cursors of transition metal containing heterogeneous catalysts, allowing homogeneous distribution of these metals inside the structure of the precursors [1]. Upon calcination and reduction these materials can give rise to well dispersed and stable metal particles supported on a carrier, of the Mg(Al)O type, possessing basic and acid sites. The synthesis of methyl isobutyl ketone (MIBK), a product of high industrial interest, from acetone was thus described on catalysts prepared from Pd-, Co-, Ni-containing LDH [2–4]. The performances first depend on the fine tuning between the acid–basic and hydrogenating properties. This can be understood considering the simplified reaction scheme shown in Fig. 1. This scheme has been proposed for the catalytic transformation of acetone in the presence of H₂ on Pd/Mg(Al)O prepared from Mg/Al LDH [4]. It was found that the highest selectivity to MIBK is achieved with ca. 0.2 wt.% Pd and Pd particles size ca. 3–5 nm. These optimum conditions come from a good balance between the number of basic and metallic sites on one hand, and from a topology of metallic sites which favours hydrogenation of C=C bond at the cost of C=O bonds on the other hand. It was actually postulated that the hydrogenation of C=O bond compared to C=C bond needs a larger number of neighbouring metal atoms in the active site; this is an ensemble size effect [5]. A very classical mean to decrease the number of neighbouring metal atoms in the active centre is the fabrication of alloys catalysts [5]. This can be achieved through the association of the active metal, i.d. Pd, with a lesser one, e.g. Cu. It was indeed well demonstrated that in PdCu bimetallics, Cu distributes itself in a random fashion at the Pd surface [6–11]. Though Cu has been proven to be an efficient hydrogenation component in the “one-pot” synthesis of MIBK from acetone on Cu/MgO [12], it actually becomes really active 100 K above Pd-based materials [4].

The aim of the present work was thus to investigate the potential of PdCu-based catalysts prepared from LDH precursors for the “one-pot” synthesis of MIBK from acetone in the presence of H₂. With the hope to promote the highest synergy between the various functionalities, the catalysts were elaborated according to two original approaches: (i) the deposition on Mg(Al)O of PdCu from mixed acetylacetonate [11], and (ii) the coprecipitation of Pd/Cu/Mg/Al LDH.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. LDHs precursors

The LDHs Mg/Al and Pd/Cu/Mg/Al were prepared by coprecipitation, at constant pH (~10), of a solution containing chosen amounts of the nitrate salts with a solution of NaOH (1.0 M). The addition of NaOH and pH were controlled by pH-STAT (Titrimo). The suspension was stirred overnight at 353 K before the solid was separated by centrifugation and rinsed five times with distilled water. The solids were then dried at 353 K overnight, before calcination in air flow at 723 K for 2 h. Finally, the PdCu-containing materials were reduced with H₂/N₂ (10/90, v/v) at 473 K for 5 h. These samples were labelled PdCu(y)-HT, y being the nominal Cu/Pd molar ratios of 0.25, 0.50 and 1.0.

2.1.2. Mixed Pd–Cu bis acetylacetonates

These mixed acetylacetonates were synthesized according to the method described by Renouprez et al. [11]. Pd(acac)₂ and Cu(acac)₂ (ALDRICH) were dissolved in various nominal ratios (Cu/Pd of 0.25, 0.50 and 1.0, mol/mol) in toluene, then recrystallized by slow evaporation of the solvent at 353 K, to yield Pd_xCu_{1-x}(acac)₂. The XRD patterns of the mixed complexes well correspond to those reported by Renouprez et al. [11], providing evidence that Pd and Cu are indeed together in heterobinuclear complexes.

2.1.3. Impregnated PdCu/Mg(Al)O

The as above calcined Mg/Al LDH give a Mg(Al)O mixed oxide. It was contacted with a H₂O-free toluene solution containing a dedicated amount of Pd_xCu_{1-x}(acac)₂ for 24 h. After evaporation the solid was dried at 353 K in vacuum, and calcined in air flow at 723 K for 2 h. The calcined material was reduced in diluted H₂ (H₂/N₂, 10/90) at 473 K for 5 h. They were denominated PdCu(y)/Mg(Al)O.

2.2. Characterization

The materials were characterized by X-ray diffraction (XRD), N₂ sorption, transmission electron microscopy (TEM, replica technique), temperature

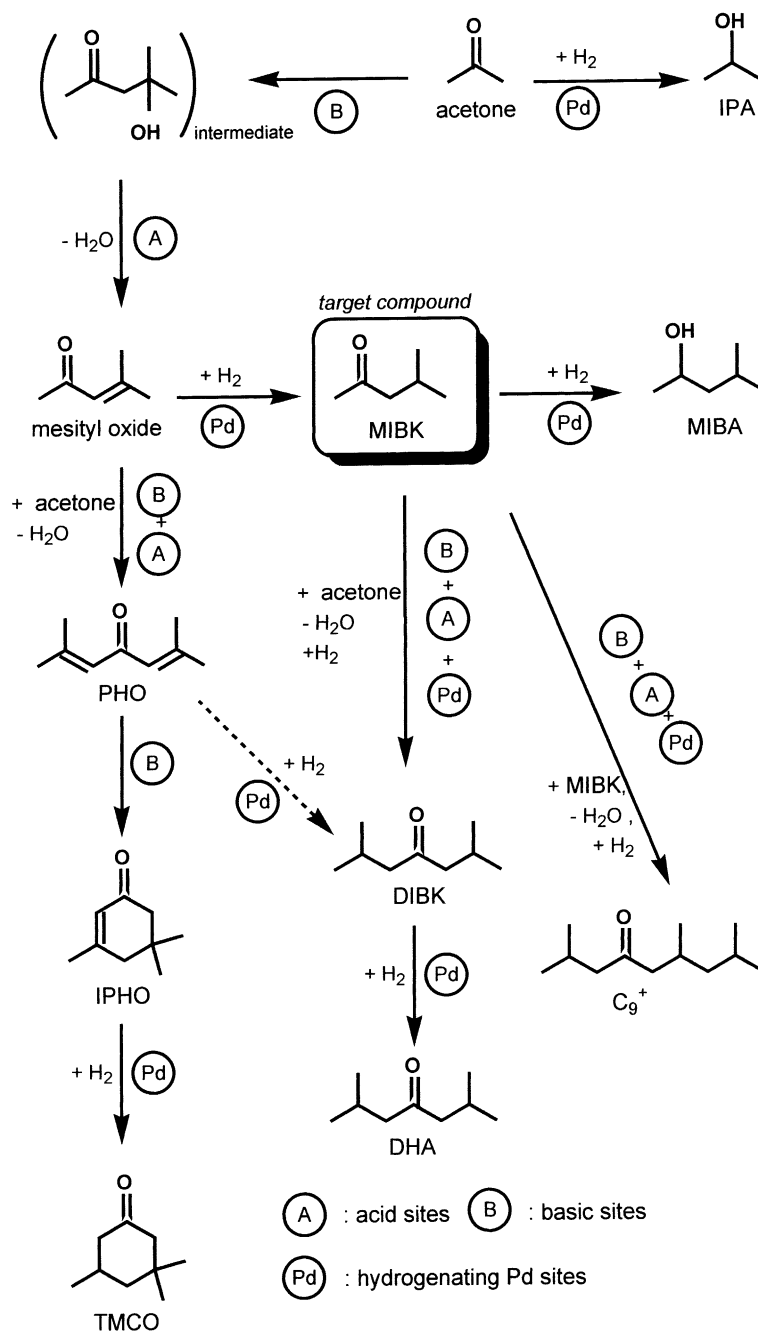


Fig. 1. Simplified scheme of the reaction of acetone with hydrogen on a solid catalyst containing basic, acid and metallic sites.

programmed reduction by H₂ (TPR), H₂ chemisorption, temperature programmed desorption of NH₃ (NH₃-TPD), and CO₂ adsorption followed by microcalorimetry and gravimetry (CO₂-TG-DSC).

Chemical analyses of the samples were performed at the Service Central d'Analyse du CNRS (Verneison, France). XRD patterns were recorded on a CGR Theta 60 instrument using Cu K α radiation. N₂ sorption experiments at 77 K were carried out with a Micromeritics ASAP 2000 instrument, and specific surface areas calculated using the BET method. The homogeneity of the metal particles size was examined by transmission electron microscopy (TEM) using a JEOL 100CX microscope.

TPR by H₂ (H₂/Ar: 3/97, flow = 30 cm³ min⁻¹, m = 30 mg, ramp = 10 K min⁻¹) was carried out with a Micromeritics AutoChem 2910 apparatus using TCD detection. The H₂ consumption was determined after trapping H₂O at ca. 200 K.

The accessibility to Pd⁰ phase was estimated by volumetry of H₂ chemisorption with a Micromeritics ASAP 2010 and using the method proposed by Benson et al. [13], which allows to eliminate the contribution from the β -PdH phase in the H₂ uptake. The sample was reactivated at 473 K in H₂ for 2 h, then outgassed at the same temperature for 1 h at 10⁻⁴ Pa. A first H₂ isotherm was determined at 313 K still 40–50 kPa by pulsing ultrapure H₂ (purity > 99.995%). After evacuation for 20 min at 10⁻⁴ Pa and 313 K, a second H₂ isotherm was determined in the same conditions as the first. The H₂ taken up by the Pd surface was estimated by the extrapolation to zero pressure of the difference between the two isotherms.

NH₃-TPD experiments were carried out with a home-made set-up using conductivity detection. The samples (m = 60 mg) were previously out gassed at 723 K, then cooled at 373 K, and contacted with NH₃ vapour. After the sample was purged for 7 h, the temperature was increased to 723 K (ramp = 10 K min⁻¹) in He (purity > 99.995%, flow = 30 cm³ min⁻¹); the evolved ammonia was trapped in a HCl solution and finally titrated.

Integral heats of CO₂ adsorption were determined with a SETARAM TG-DSC-111 apparatus. The sample was first reactivated in He at 623 K and further cooled and maintained at 373 \pm 0.01 K in He. CO₂ was then fed to the sample and the weight uptake and thermal event were recorded simultaneously.

2.3. Catalytic tests

The catalytic tests were performed under atmospheric pressure in a microflow fixed-bed reactor (6 mm i.d.) using 50–100 mg of catalyst (grain size: 63–125 μ m). Prior to any measurements, the catalysts were submitted to in situ activation in H₂ at 473 K for 12 h (ramp: 2 K min⁻¹). Acetone was fed by bubbling H₂/He mixture through a saturator at 273 K ($P(\text{acetone}) = 8.4 \text{ kPa}$). The reaction mixture (H₂/He/acetone = 46/46/8, flow = 60 cm³ min⁻¹) was then passed through the catalyst at 423 K and the effluent sampled at regular time intervals for analysing on line with a gas chromatograph (Carlo Erba) equipped with a capillary column (30 m \times 0.53 mm i.d., Carbowax 20M bonded phase) and a flame ionisation detector. All connecting lines, commutation and sampling valves were placed in a hot box heated at 393 K in order to prevent any condensation. The following parameters were determined to evaluate the catalytic properties:

$$\begin{aligned} \text{acetone conversion (mol\%)} \\ = \frac{\text{acetone}_{\text{in}} - \text{acetone}_{\text{out}}}{\text{acetone}_{\text{in}}} \times 100 \end{aligned}$$

$$\begin{aligned} \text{selectivity in product } i \text{ (mol\%)} \\ = \frac{(\text{corrected area})_i}{\text{sum of all corrected areas of products}} \times 100 \end{aligned}$$

The selectivities have been calculated from peak areas taking into account the different response factors in the flame ionisation detector. At high conversion of acetone, the carbon balance was equilibrated at $\pm 2\%$.

In the course of the reaction of acetone with hydrogen, we detected 2-propanol (IPA), 4-methyl-2-pentanone (MIBK), 2,6-dimethyl-4-heptanone (DIBK) as main products, and 2,6-dimethyl-4-heptanol (DHA), 3,5,5-trimethyl-2-cyclohexen-1-one (IPHO), 3,3,5-trimethyl-cyclohexanone (TMCO), 4-methyl-2-pentanol (MIBA) and 2,6,8-trimethyl-4-nonanone (TMNO) as secondary and trace products. The nature of the products was determined by comparing the retention times with standard samples and also by GC-MS coupling.

3. Results and discussion

Table 1 gives the chemical composition of the precursors of the catalysts, the Pd and Cu contents in the final reduced materials, and the specific surface area. XRD patterns demonstrate that all the samples exhibit the HDL structure before activation, which transforms into the mixed oxide structure upon calcination and reduction. The porous textures of the final catalysts are very similar, with specific surface ranging from 226 to 270 m² g⁻¹.

A key point to understand the catalytic behaviour deals with some identification of the acid–basic and hydrogenating functions of the materials. This was achieved by CO₂–TG–DSC and NH₃–TPD for the probe of basic and acid sites, respectively.

The integral heat of CO₂ adsorption ($\Delta H_{\text{CO}_2} = 70\text{--}80\text{ kJ mol}^{-1}$) and the number of basic sites which adsorb one CO₂ molecule ($n_{\text{CO}_2} = (2.1\text{--}6) \times 10^{20}$ sites g⁻¹) (Table 2) exhibit some small changes from sample to sample without any clear correlation in comparison with the chemical composition. Besides, the amounts of CO₂ adsorbed correspond to a standard density of basic sites in such of solids after calcination at 723 K [14].

Regarding NH₃–TPD (Fig. 2), the profiles are identical whatever the samples with NH₃ desorption at low temperature (maximum around 523 K) which indicates weak acid strength. The amounts of NH₃ desorbed are 0.19 ± 0.06 mmol g⁻¹. As a whole, the acidity exhibited by the samples is weak [14]. Globally, one can conclude that no large difference in acid–base properties exists between these catalysts.

The metallic function was studied by TPR, H₂ chemisorption and TEM examination. TPR experiments provide information about the reducibility of Pd and Cu phases, which depends on the degree of mutual interaction between Pd and Cu on the one hand, and with the support on the other hand. Fig. 3 shows the TPR profiles of the calcined materials. These profiles are only shown at $T < 473$ K where the reduction of the Pd and PdCu oxides takes place. There are also large consumptions of H₂ above 573 K which corresponds to the reduction of remaining nitrates anions, as mass spectrometry coupling has demonstrated. With Pd-HT and Pd/Mg(Al)O, there is a negative peak at ca. 333 K which corresponds to hydrogen liberated during Pd hydride decomposi-

tion, since PdO reduction occurs mainly below room temperature [15]. However, a small H₂ consumption with Pd-HT can be identified at 373 K, which may correspond to the reduction of Pd species in stronger interaction with the support. This feature appears with Pd-HT prepared by co-precipitation, for which an intimate contact between Pd, Mg and Al may be expected.

With PdCu-based samples, the negative peak at 333 K tends to disappear, because a small amount of Cu inhibits the formation of the Pd hydride phase [16]. This is a strong indication that Pd and Cu are together in bimetallic aggregates. Moreover, there is a second peak of H₂ consumption of larger intensity in the domain 380–420 K which could correspond to the reduction of PdCuO_x mixed oxides. CuO alone is indeed reduced at 500–570 K depending on the size of CuO aggregates and the support [17]. More precisely, the TPR profiles of PdCu precursors exhibit slightly different shapes. For the PdCu(y)-HT, there is a first peak around 373 K which could correspond to PdO aggregates in strong interaction with the support and a second component of much larger intensity appears with a maximum at 398–403 K corresponding to PdCuO_x entities. The H₂ taken up during these two reduction steps corresponds to $\text{H}_2/(\text{Pd} + \text{Cu}) = 0.75\text{--}1.1$ (Table 2). Though the signal to noise ratio and the resolution were poor, due to the low metal content, one can conclude that Pd and Cu are (i) reduced below 473 K, and (ii) probably involved in bimetallic PdCu entities which largely prevail. The latter are even the only occurring species with a very broad reduction peak at ca. 350–450 K for the impregnated PdCu(y)/Mg(Al)O. This is satisfying since these materials were prepared from heterobinuclear complexes Pd_xCu_{1-x}(acac)₂.

The H₂ chemisorption and TEM examinations were only carried out on Pd-HT, Pd/Mg(Al)O, PdCu(0.25)-HT and PdCu(0.25)/Mg(Al)O which exhibited the most interesting catalytic properties to be discussed (vide infra). The accessibility to the Pd phase (H/Pd) is given in Table 3. H/Pd is of 0.30–0.35 for the impregnated samples, but extremely low (<0.02) for the co-precipitated ones. The TEM examinations of the samples are exemplified by some micrographs in Fig. 4; the size distributions are homogeneous and narrow. The mean diameter (in surface) is given in Table 3. They are of 2.1 nm for the

Table 1
Chemical compositions and formula of the precursors, Pd (wt.%) and Cu (wt.%) and specific surface area of the catalysts

Sample	Chemical composition of the precursor (wt.%)						Formula	Pd (wt.%)	Cu (wt.%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
	Mg	Al	Pd	Cu	N	C				
Pd/Mg(Al)O ^a	21.33	8.42	–	–	3.29	0.26	$\text{Mg}_{0.74}\text{Al}_{0.26}(\text{OH})_2(\text{CO}_3^{2-})_{0.018}(\text{NO}_3^-)_{0.20}$	0.24	–	226 ^b
PdCu(0.25)/Mg(Al)O								0.24	0.03	
PdCu(0.50)/Mg(Al)O								0.20	0.05	
PdCu(1.0)/Mg(Al)O								0.20	0.09	
Pd-HT	23.69	9.97	0.19	–	3.09	1.12	$\text{Mg}_{0.72}\text{Pd}_{0.0013}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3^{2-})_{0.069}(\text{NO}_3^-)_{0.16}$	0.31	–	243
PdCu(0.25)-HT	20.92	8.35	0.15	0.04	3.40	0.47	$\text{Mg}_{0.73}\text{Pd}_{0.0012}\text{Cu}_{0.0005}\text{Al}_{0.26}(\text{OH})_2(\text{CO}_3^{2-})_{0.033}(\text{NO}_3^-)_{0.21}$	0.24	0.06	257
PdCu(0.50)-HT	20.76	8.47	0.17	0.06	3.30	0.47	$\text{Mg}_{0.73}\text{Pd}_{0.0014}\text{Cu}_{0.0008}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3^{2-})_{0.033}(\text{NO}_3^-)_{0.20}$	0.27	0.12	252
PdCu(1.0)-HT	20.57	8.77	0.16	0.13	3.05	0.53	$\text{Mg}_{0.72}\text{Pd}_{0.0013}\text{Cu}_{0.0017}\text{Al}_{0.28}(\text{OH})_2(\text{CO}_3^{2-})_{0.038}(\text{NO}_3^-)_{0.19}$	0.28	0.22	270

^a The chemical composition is that of the precursor of the Mg(Al)O support.

^b The surface area is that of the Mg(Al)O support.

Table 2

Integral heat of CO₂ adsorption and amount of CO₂ adsorbed in CO₂-TG-DSC experiments, amount of NH₃ desorbed in NH₃-TPD experiments, and H₂ consumption in TPR experiments

Samples	CO ₂ ($\times 10^3$ mol g ⁻¹)	$-\Delta H_{\text{CO}_2}$ (kJ mol ⁻¹)	NH ₃ ($\times 10^3$ mol g ⁻¹)	H ₂ /(Pd + Cu) (mol/mol)
Pd/Mg(Al)O ^a	0.29	55	0.18	0.70
PdCu(0.25)/Mg(Al)O	0.46	67	0.17	0.80
PdCu(0.50)/Mg(Al)O	0.35	75	0.16	0.80
PdCu(1.0)/Mg(Al)O	0.59	70	0.16	0.90
Pd-HT	0.53	76	0.24	0.70
PdCu(0.25)-HT	0.49	76	0.24	0.75
PdCu(0.50)-HT	0.60	72	0.20	1.10
PdCu(1.0)-HT	0.44	74	0.13	0.70

^a The chemical composition is that of the precursor of the Mg(Al)O support.

impregnated samples and of 4.1–4.5 nm for the coprecipitated ones. An empirical relationship is often used for estimating the mean particle size from the value of dispersion (H/Pd) for monometallic catalysts: d_p (nm) $\cong 1.1/(H/Pd)$. It comes out that the mean particle size should be of 3.1 nm for Pd/Mg(Al)O, which is in satisfying agreement with the value from TEM. In contrast, there is a full disagreement for Pd-HT since

the mean size derived from chemisorption would be 10 times larger (55 nm compared to 4.1 nm). Since the Pd phase is practically fully reduced (Table 2), one should conclude that a large part of the surface of Pd particles is inaccessible to hydrogen. A model of metal particles decorated with confettis of, e.g. MgAlO_x can thus be proposed (Fig. 5), which looks very similar with that of Pt/TiO₂ in strong metal support

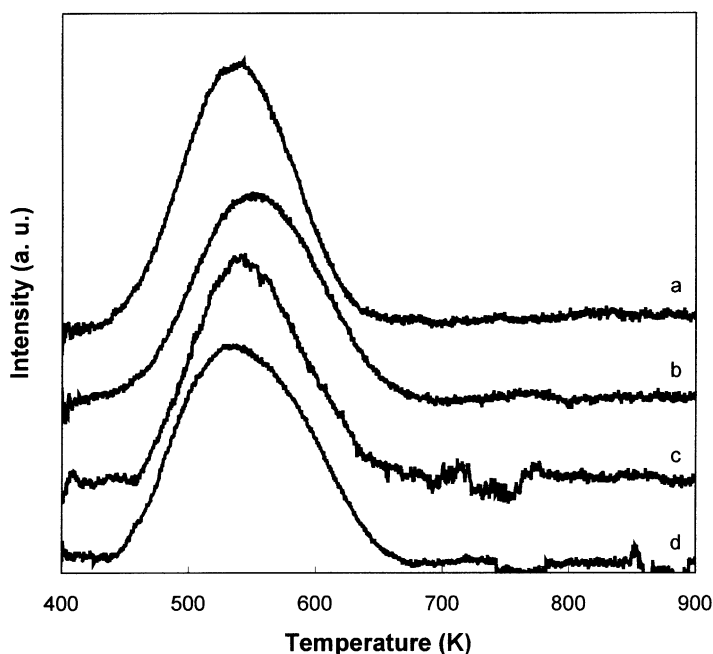


Fig. 2. NH₃-TPD profiles of impregnated PdCu-based catalysts (ramp: 10 K min⁻¹): (a) PdCu(1.0)/Mg(Al)O; (b) PdCu(0.50)/Mg(Al)O; (c) PdCu(0.25)/Mg(Al)O; (d) Pd/Mg(Al)O.

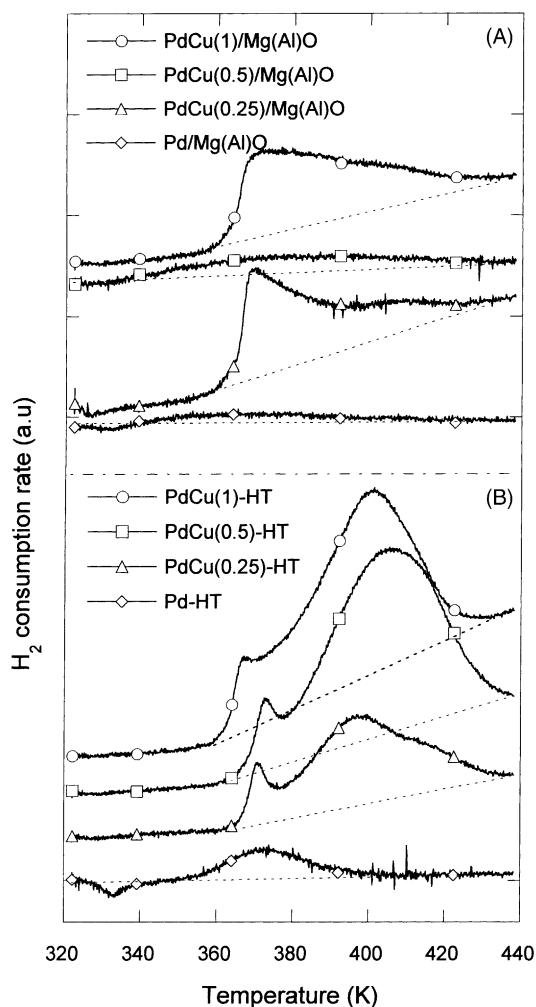


Fig. 3. H_2 -TPR profiles of the calcined catalysts: (A) impregnated catalysts; (B) coprecipitated catalysts. Conditions: H_2/Ar , 3/97; ramp, 10 K min^{-1} .

interaction [18]. In such a model, 90–95% of the Pd surface would thus be blocked.

The time history plots of the activity are shown in Fig. 6. As compared to a previous report [4], the present Pd/Mg(Al)O sample is slightly more active. This behaviour is originated from the difference of calcination temperature of Mg(Al)O, very likely. It is well known that the total basicity of Mg(Al)O mixed oxides goes through a maximum value upon calcination at 823 K [19] whereas in the previous report [4] Mg(Al)O was calcined at 623 K. Globally, the sam-

Table 3

Accessibility to Pd and mean particle size from H_2 chemisorption and TEM examination

Sample	H/Pd	dp (nm)	
		From H_2 chemisorption	From TEM ^a
Pd/Mg(Al)O ^a	0.35	3.1	2.2
PdCu(0.25)/Mg(Al)O	0.30	–	2.1
Pd-HT	0.02	55	4.1
PdCu(0.25)-HT	0.01	–	4.5

^a 500–600 particles have been examined.

ples prepared by impregnation of Mg(Al)O are most stable than the coprecipitated ones. One can even say that Pd/Mg(Al)O and PdCu(0.25)/Mg(Al)O are very stable over 6 h in stream. In contrast, PdCu(0.25)- and PdCu(0.5)-HT exhibit fast deactivation. The reason is not clear for the latter, but can be understood for the former considering the high selectivity to IPHO. This is indicative of a deficit of the metal function with respect to the basic one: the condensation of mesityl oxide with acetone is faster than its hydrogenation to MIBK (Fig. 1) [4]. In this context, IPHO and/or TMCO are the only identified by-products, but heavier compounds are also formed which remain adsorbed on the catalyst, decreasing thus its activity.

On most of the samples, the initial activity is ca. 30–45%, when the accessibility to the Pd surface varies by a factor larger than 10 (Table 3), but the basicity stays comparable (Table 2). One can thus conclude that the rate determining step is probably the base catalysed condensation. More precisely, the slight variations of initial activity between the different samples could be accounted for by some changes in the basicity of the surface, which depends on the number and strength of basic sites (see Table 2).

The catalytic properties after 6 h of reaction are listed in Table 4. Whatever the sample series, impregnated or coprecipitated, the association of Cu to Pd has little effect on the selectivity. Even though, one may identify a slight decrease of hydrogenated compounds (IPA and MPA) on the PdCu/Mg(Al)O samples in comparison with Pd/Mg(Al)O. The objective of reducing the hydrogenation capacity of C=O bonds by alloying Pd has not then succeeded significantly, so that Pd and Cu are very likely together in the same bimetallic aggregates (vide supra). In con-

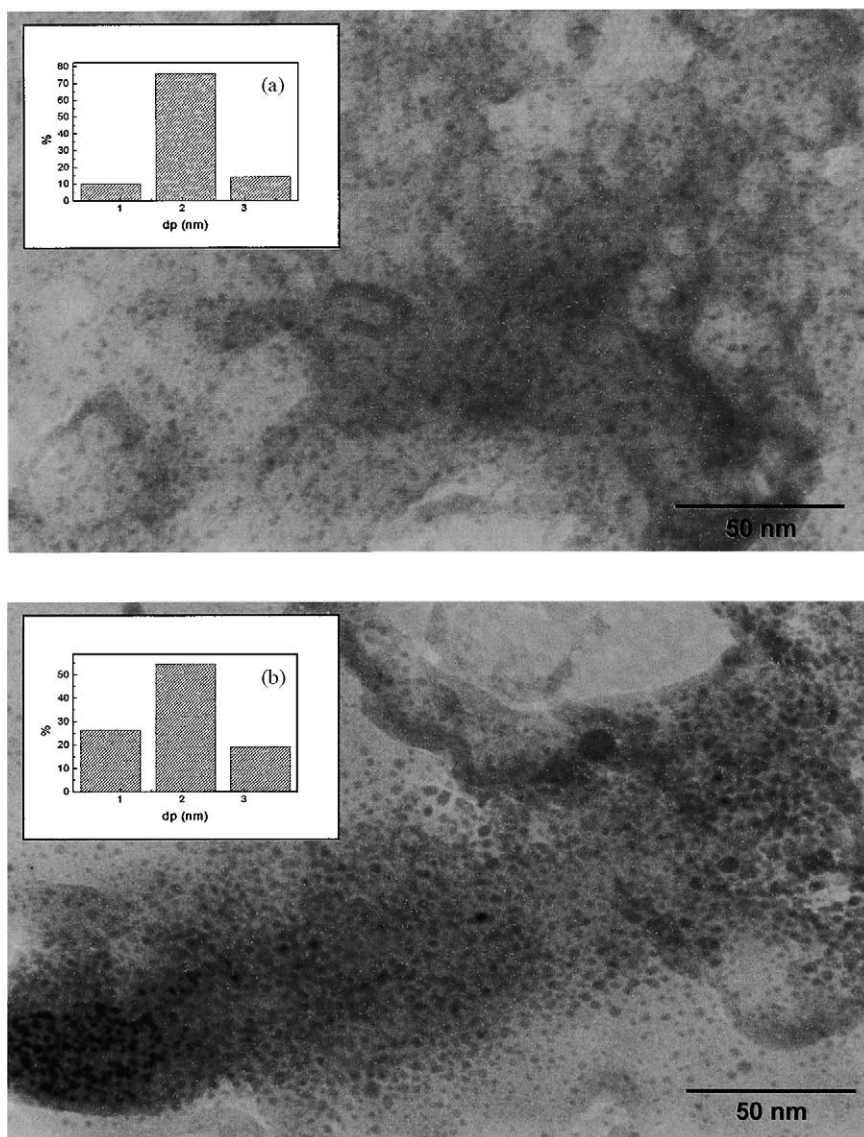


Fig. 4. TEM micrographs and particle size histograms of (a) Pd/Mg(Al)O; (b) PdCu(0.25)/Mg(Al)O; (c) Pd-HT; (d) PdCu(0.25)-HT.

trast, the method to prepare the samples has a strong influence on the selectivity. The rate of C=O bond hydrogenation appears 10-fold lower for the coprecipitated samples. That allows to reach a selectivity larger than 90% to MIBK + DIBK with the Pd-HT catalyst.

From the characterization of the various catalysts, a model was proposed to feature the coprecipitated catalysts (Fig. 5). In this model the topology of the surface

of metal particles looks very different as compared to that of impregnated samples. There is an extended dilution of the Pd surface by the decorating MgAlO_x species. The resulting very small ensembles of a few Pd atoms hydrogenate the C=C bond much faster than the C=O bond. The achievement of reduction of the C=O bond hydrogenation has been thus fulfilled not through alloying Pd with Cu, but by some kind of metal support interaction.

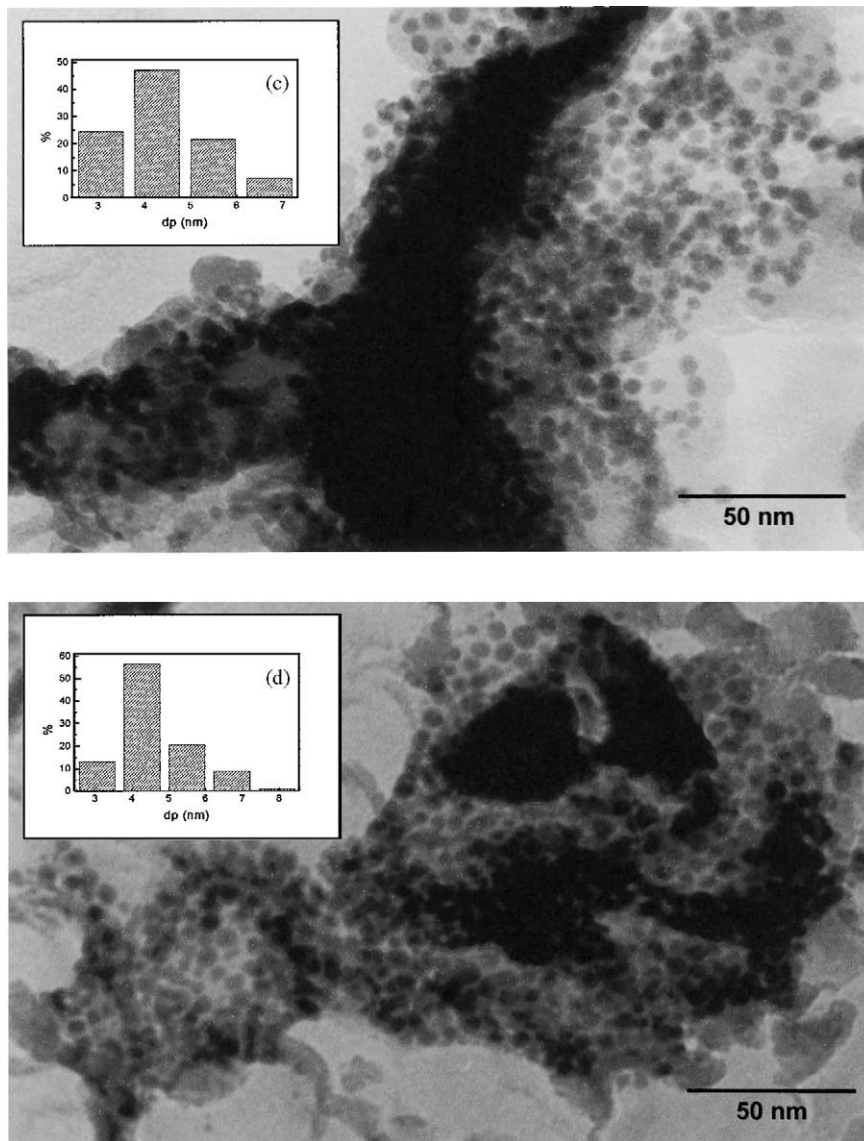


Fig. 4. (Continued).



Fig. 5. Models of Pd/Mg(Al)O and Pd-HT catalysts.

Table 4

Catalytic properties after 6 h in stream of some PdCu-based catalysts in the transformation of acetone in presence of hydrogen^a

Sample	Conversion (mol%)	Selectivity (mol%)						
		IPA	MIBK	MPA	DIBK	DHA	IPHO	TMCO
Pd/Mg(Al)O	38	19.8	46.2	2.8	22.7	1.3	6.2	0.8
PdCu(0.25)/Mg(Al)O	32	12.8	52.9	1.9	23.8	1.3	6.7	0.4
PdCu(0.50)/Mg(Al)O	24	16.5	53.9	1.9	20.0	1.3	5.8	0.3
PdCu(1.0)/Mg(Al)O	31	12.0	57.5	1.6	23.5	1.2	3.2	0.4
Pd-HT	35	3.4	67.3	1.5	23.3	1.5	3.0	–
PdCu(0.25)-HT	10	1.1	54.2	3.1	11.5	1.6	28.4	–
PdCu(0.50)-HT	10	2.5	72.0	1.7	15.6	1.8	6.7	–
PdCu(1.0)-HT	28	5.8	60.0	0.9	26.1	1.8	5.4	–

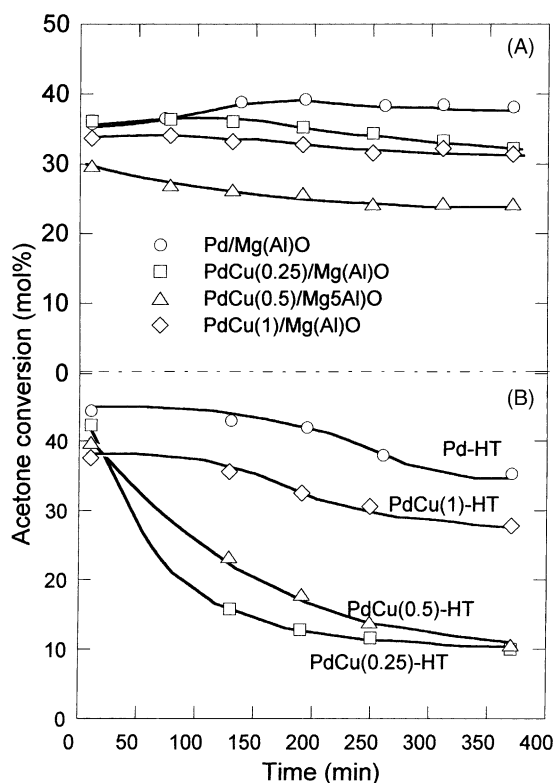
^a Conditions: $T_R = 423$ K, acetone/H₂ = 0.17, WHSV = 5 h⁻¹.

Fig. 6. Time history plots of ACE conversion on the (A) impregnated, and (B) coprecipitated catalysts.

4. Conclusions

We intended in the present work to design new Pd-LDH catalysts exhibiting higher selectivity in the

“one-pot” synthesis of MIBK from acetone. From previous works we thought to achieve this goal through alloying Pd with Cu. Actually, we have succeeded thanks to the one step synthesis of Pd(Cu)-containing LDHs materials. Their activation by calcination and reduction leads to well dispersed PdCu particles supported on Mg(Al)O. The metallic particles in these catalysts are in “strong” interaction with the support. The surface of the 4 nm sized particles is extensively decorated with migrating MgAlO_x species. This results in a dilution of the metal surface in very small ensembles of a few metal atoms, less prone to hydrogenate the C=O bonds, but keeping its full capacity for hydrogenating the C=C bonds of the α,β -unsaturated carbonyls intermediates. A selectivity higher than 90% in MIBK + DIBK can thus be obtained. That could be attractive since MIBK + DIBK mixtures of various compositions are used as solvent.

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