Influence of the metal function in the “one-pot” synthesis of 4-methyl-2-pentanone (methyl isobutyl ketone) from acetone over palladium supported on Mg(Al)O mixed oxides catalysts

Nigamananda Das *, Didier Tichit, Robert Durand, Patrick Graffin and Bernard Coq **

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS, ENSCM, 8, rue de l’Ecole Normale,
34296 Montpellier Cedex 5, France

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Pd/Mg(Al)O samples ($0.05 < \mathrm{Pd} < 0.5$ wt%) were evaluated in the gas phase reaction of acetone with hydrogen to methyl isobutyl ketone (MIBK). The catalysts were prepared by impregnating a calcined Mg–Al layered double hydroxide with Pd acetylacetonate in toluene solution. The highest selectivity to MIBK was achieved with ca. 0.2 wt% Pd and size of Pd particles of ca. 3–5 nm.

KEY WORDS: methyl isobutyl ketone; acetone; Pd; layered double hydroxides; multifunctional catalysis

1. Introduction

Several recent reports have put in evidence the potential of multifunctional solid catalysts, exhibiting acid–base and hydrogenating properties, for the ketones and aldehydes condensation to higher homologues [1–12]. This is particularly true for materials prepared from layered double hydroxides (LDH) as precursors [9,11]. A very typical example is the “one-pot” synthesis of acetone to 4-methyl-2-pentanone (methyl isobutyl ketone), product of high industrial interest. This could constitute an economically viable alternative to the classical three-step catalytic process, still industrially used. In the three-step process, the acetone is condensed to diacetone alcohol with soda; diacetone alcohol is in turn dehydrated to mesityl oxide on acid catalyst which is finally hydrogenated to methyl isobutyl ketone. A problem associated with this approach is the unfavorable thermodynamic equilibrium of the first condensation step. Moreover, the use of a solid base catalyst, replacing soda, will promote an eco-friendly process.

Some problems associated with the “one-pot” process are the lifetime of the catalyst and the methyl isobutyl ketone yield; aging of the catalyst is due to sintering of the metal and/or fouling by the by-products formed. It was proposed that the catalytic properties are very dependent on the balance between metallic and basic functions [9,10]. In this work, part of studies devoted to the exploration of LDH-based materials as precursors for multifunctional catalysts, the main attention is focussed on the influence on the catalytic properties of the metallic function, with respect to the metal dispersion. As the aim is to promote C=C bond hydrogenation prior to that of C=O bond, occurring in hydrogenation of ketones to alcohols and of α,β-unsaturated ketone (mesityl oxide) to unsaturated alcohol, palladium was chosen as the metal function [13–15].

In LDH-based materials, the basic property depends on the chemical composition and the activation treatments [16]. For the present study, we have chosen the Mg/Al LDH (hydrotalcite) with Mg/Al molar ratio of three and calcined at 623 K. The resulting Mg(Al)O material exhibits the structure of mixed oxide with a high number of basic sites of medium strength [16]. In order to maintain the basic function almost the same whatever the metal content in the various Pd/Mg(Al)O samples, Pd was introduced through Pd-acetylacetonate impregnation in water-free toluene solution. This procedure will avoid the possible reconstruction of the layered structure of the support and changes in acid–base properties [17].

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Hydrotalcite

The hydrotalcite was prepared by coprecipitation, at constant pH (∼10), of a solution of $Mg(NO_3)_2{\cdot}6H_2O$ (0.3 mol) and $Al(NO_3)_3{\cdot}6H_2O$ (0.1 mol) with a solution of NaOH (1.0 M). The addition of NaOH and the pH were controlled by pH-STAT (Titrino). The suspension was stirred overnight at 353 K before the solid was separated by centrifuge and rinsed five times with distilled water. Exchange of NO_3^- ions by CO_3^{2-} was done suspending the solid in 0.1 M Na_2CO_3 twice. The final exchanged product was filtered, washed thoroughly with distilled water and dried overnight at 353 K.

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[*] Present address: Department of Chemistry, Godda College, Godda 814 133, Bihar, India.

[**] To whom correspondence should be addressed.

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2.1.2. Pd/Mg(Al)O

The carbonate-exchanged hydrotalcite was heat-activated in air flow at 623 K for 4 h to yield the mixed oxide Mg(Al)O. After cooling to room temperature the solid was contacted with a H_2O-free toluene solution containing a dedicated amount of palladium acetylacetonate ($Pd(acac)_2$, Strem Chemicals) for 12 h. After evaporation the solid was dried at 353 K in vacuum, and calcined in air flow at 623 K for 4 h. The calcined material was reduced in diluted H_2 (H_2/N_2 10/90) at 473 K for 5 h (flow 60 $cm^3\,min^{-1}\,g^{-1}$, ramp 0.5 $K\,min^{-1}$). Several samples containing 0.05, 0.1, 0.2 and 0.5 wt% Pd were prepared; they were denominated PdCHT05, PdCHT1, PdCHT2, PdCHT5, respectively.

2.2. Characterization

The solids were characterized with a wide variety of techniques involving X-ray diffraction (XRD), N_2 sorption, transmission electron microscopy (TEM), H_2 chemisorption, thermo-gravimetry, calorimetry of CO_2 adsorption.

Chemical analyses of the samples were performed at the Service Central d'Analyse du CNRS (Vernaison, France). XRD patterns were recorded on a CGR Theta 60 instrument using Cu K_α radiation. N_2 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.

H_2 chemisorption was carried out by the pulse technique with a Micromeritics AutoChem 2910 apparatus. After reactivation at 473 K in H_2 for 4 h, the sample was cooled in Ar, then maintained at 323 ± 0.01 K. Pulses of 500 μl of H_2/Ar (3/97, ultrahigh purity gases) were fed to the sample till completion of the chemisorption. 10 min of equilibration are allowed after each pulse. This procedure can be compared to the adsorption–back-sorption isotherm method proposed by Benson et al. [18] to eliminate the contribution from the β-PdH phase in the H_2 uptake. This phase cannot maintain in the pure Ar feed between the pulses and the final 20 min equilibration after the last pulse.

Integral heats of CO_2 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 ± 0.01 K in He. CO_2 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 0.063–0.125 μm). Prior to any measurements, the catalysts were subjected to *in situ* activation in H_2 at 473 K for 12 h (ramp 2 $K\,min^{-1}$). Acetone was fed by bubbling H_2/He mixture through a saturator at 273 K ($P_{acetone} = 8.4$ kPa). The reaction mixture was then passed through the catalyst and the effluent sampled at regular time intervals for analyzing on line with a gas chromatograph (Carlo Erba) equipped with a capillary column (30 m × 0.53 mm i.d., Carbowax 20M bonded phase) and a flame ionization 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:

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

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

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

In the protocol for the catalytic tests, reaction was first carried out for 12 h at 473 K (He/H_2/acetone = 46/46/8 (v/v/v), flow = 60 $cm^3\,min^{-1}$) before reaching a nearly steady state activity ("stabilisation" period). The reaction temperature was then varied from 423 to 473 K, by alternating high and low values, and then the feed composition was also varied at 448 K. In the course of the reaction of acetone with hydrogen, we detected propan-2-ol (IPA), 4-methyl-2-pentanone (MIBK), 2,6-dimethyl-4-heptanone (DIBK) as main products, and 4-methyl-3-penten-2-one (MO), 3,5,5-trimethyl-2-cyclohexen-1-one (IPHO), 3,3,5-trimethylcyclohexanone (TMCO), 4-methyl-pentan-2-ol (MIBA) and 2,6,8-trimethylnonan-4-one (C_{9+}) as secondary 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

The Mg/Al LDH dried at 353 K exhibits the XRD pattern of hydrotalcite. Upon calcination at 623 K, the layered compound transforms into the mixed oxide Mg(Al)O, with a surface area of 217 $m^2\,g^{-1}$. The surface area values do not change much (∼220–230 $m^2\,g^{-1}$) upon subsequent introduction of Pd.

Table 1 presents some characteristics of the catalysts and the activity on the fresh and stabilized samples. These data call forth some comments:

(1) As expected, the accessibility of Pd, derived from the uptake of irreversibly adsorbed hydrogen ($D = Pd_{surf.}/Pd_{tot.} \approx H/Pd$, assuming a chemisorption stoichiometry $H_{ad}/Pd_s = 1$ [18]), decreases when the Pd content increases. This is confirmed by TEM micrographs, which show a concurrent increase of the mean particle size. However, the size of Pd particles appears slightly smaller in TEM examinations than expected

Table 1
Some characteristics and catalytic properties of the Pd/Mg(Al)O catalysts.

Sample	Pd (wt%)	H/Pd	Pd_s ($mol\,g_{cat}^{-1}$) $\times 10^6$	n_{CO_2} ($mol\,g^{-1}$) $\times 10^4$	ΔH_{CO_2} ($kJ\,mol^{-1}$)	α_0[a] (mol%)	α_{12}/α_0[a]	Rate[a] ($mol\,g^{-1}\,h^{-1}$)
Mg(Al)O	–	–	–	6.9	83.4	–	–	–
PdCHT05	0.05	0.70	3.5	6.8	80.5	11.9	0.17	0.007
PdCHT1	0.1	0.30	3.0	6.8	82.2	16.8	0.38	0.022
PdCHT2	0.2	0.20	4.0	6.2	81.8	40.0	0.48	0.07
PdCHT5	0.5	0.15	7.5	6.4	83.9	59.0	0.50	0.1

[a] α_0, α_{12} and the rate were determined at 473 K.

from H_2 chemisorption by application of the very rough empirical relationship $d_p(\mathrm{nm}) = 1/D$. Otherwise, TEM examinations provide evidence of a good homogeneity in the size distribution. It is important to keep in mind that PdCHT05, PdCHT1 and PdCHT2 which exhibit similar number of surface Pd atoms, obtained from the total number of Pd atoms and the Pd dispersion D, differ clearly by the size of the metal particles.

(2) The integral heat of CO_2 adsorption ($\Delta H_{CO_2} = 80$–$84\ kJ\,mol^{-1}$) and the number of basic sites which adsorb one CO_2 molecule ($n_{CO_2} = 6$–7×10^{-4} site g^{-1}) are more or less identical for all the samples (table 1). From these observations it is evident that the introduction of Pd in small amount through $Pd(acac)_2$ from H_2O-free toluene solution has maintained the acid–base properties properly identical.

(3) The initial activity (α_0) and the relative activity after 12 h under stream (α_{12}/α_0), at 473 K, increase with the Pd content in the catalysts. As a consequence, the activity is 15 times larger on PdCHT5 than on PdCHT05 after 12 h "stabilisation". Such a behavior had also been previously reported in the reaction of acetone and H_2 over Cu/MgO [10]. There are also some fluctuations in the products distribution during the "stabilisation" step of the catalysts.

It is expected that changes in Pd content, contact time, feed composition and reaction temperature alter the distribution of products. The most important one is the change of catalytic properties as a function of Pd content. This is shown in figure 1 for the reaction carried out at 473 K. First of all, one should precise that the activity is low and the deactivation very fast on Pd-free Mg(Al)O, MO and IPHO being the only products identified in significant amounts. Introduction of Pd in the catalyst results in the formation of products involving a hydrogenation step. However, clear differences appear depending on the amount of added Pd:

(i) MO is still present in large quantity at 0.05 wt% Pd, but totally disappears at 0.2 wt% Pd;

(ii) the selectivity to TMCO goes through a maximum at 0.1 wt% Pd;

(iii) the selectivity to IPA steadily increases with the Pd content; and

(iv) the selectivity to DIBK becomes significant at 0.2 wt% Pd.

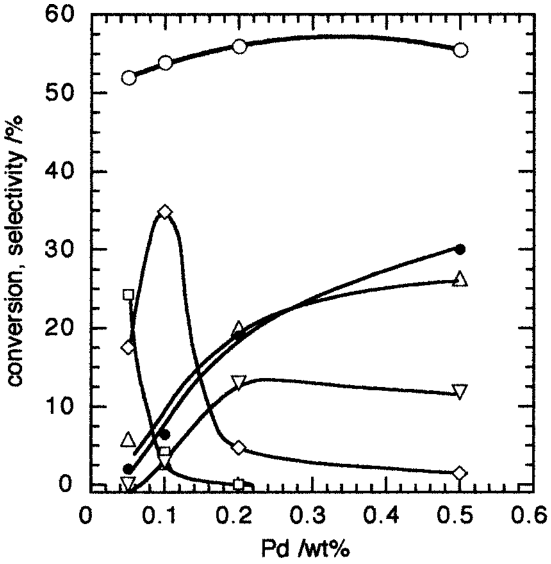

Figure 1. Conversion of acetone (●) and products distribution as a function of the Pd content in the catalysts; $T_R = 473$ K, acetone/$H_2 = 0.17$, WHSV $= 5\ h^{-1}$; (△) IPA, (□) MO, (○) MIBK, (▽) DIBK and (◇) TMCO, selectivities to MIBA and C_{9+}: 1–3% both.

In all cases, the selectivity to MIBK, the target compound, does not change much and varies in the range 52–55%.

The reactants ratio, acetone/H_2 ($0.14 \leqslant$ acetone/$H_2 \leqslant 0.55$), has a great influence on the distribution of products, as depicted in figure 2 for PdCHT2 catalyst at the reaction temperature of 448 K. It is evident that a high acetone/H_2 ratio always favors the formation of MIBK as well as TMCO while decreasing the selectivity of IPA sharply. This is in agreement with the previous report on the same reaction carried out on Cu/MgO [10], where the selectivity to IPA decreased sharply (from 70% to near zero) when acetone/H_2 ratio increased from 0.12 to 0.75. A higher value of acetone/H_2 ratio ($\geqslant 1.0$) resulted in condensed products (C_{9+}) in the reactor and was avoided in the present study.

Finally, the formation of MIBK is favored by a low reaction temperature, mainly at the expense of IPA. In contrast, Chen et al. [9] identified an increase of the selectivity to both IPA and MIBK at low reaction temperature with Pd/Mg(Al)O, but with a very high acetone/H_2 ratio of 5. A five-fold increase in contact time ($5 < \mathrm{WHSV} < 25\ h^{-1}$) decreases the conversion by three, and the selectivity to IPA increases slightly whereas that to DIBK decreases, as expected.

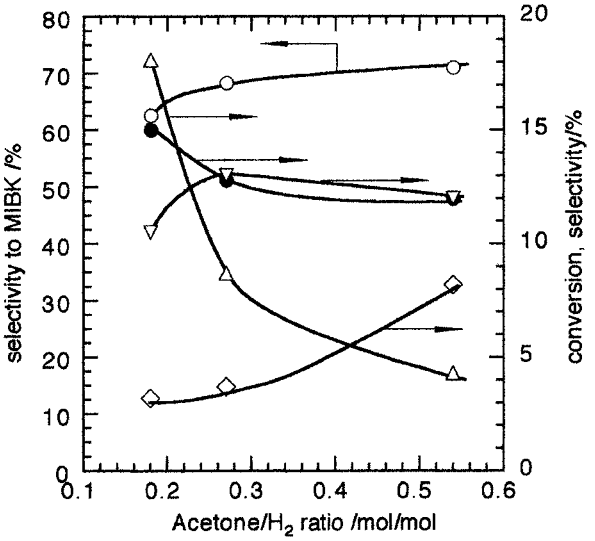

Figure 2. Conversion of acetone (●) and products distribution as a function of acetone/H_2 ratio on PdCHT2 catalyst; $T_R = 448$ K, WHSV $= 5\ \mathrm{h}^{-1}$; (△) IPA, (○) MIBK, (▽) DIBK and (◇) TMCO, selectivities to MIBA and C_{9+}: 1–3% both.

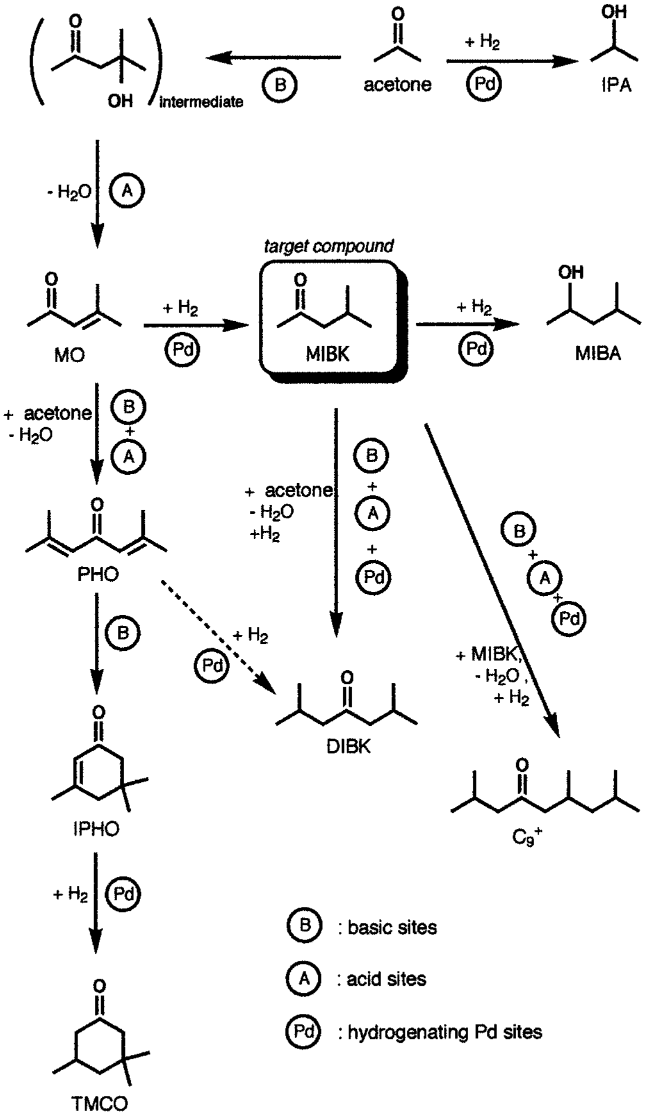

Figure 3. Simplified scheme of the reaction of acetone with hydrogen on a solid catalyst containing basic, acid and metallic sites.

In the reaction of acetone with H_2 over Pd/Mg(Al)O catalysts, a great number of products were thus identified with proportions higher than 1%. For this kind of catalysts, exhibiting basic, acid and hydrogenating sites, a reaction scheme, shown in figure 3, can be proposed in agreement with literature [7,12,19], logical chemistry and changes of selectivity with contact time. Depending on the catalyst used, all these compounds appeared, at least as trace amounts, with the exception of PHO and the intermediate diacetone alcohol. Whatever the catalyst, it is worth noting that the adsorption/desorption of CO_2 provided evidence that the basic properties of these materials are very similar (table 1). They basically differ by the metallic function.

Obviously, it comes out first that the deep hydrogenation, to saturated alcohol IPA mainly, increases with the Pd content as shown by the behavior of PdCHT5. However, the comparitive behaviors of PdCHT05, PdCHT1 and PdCHT2 are much more interesting to discuss. One should keep in mind that PdCHT05, PdCHT1 and PdCHT2, which differ in Pd content, exhibit comparable concentration of surface Pd atoms (table 1) of ca. 3.5×10^{-6}, 3×10^{-6} and $4 \times 10^{-6}\ \mathrm{mol\,g_{cat}^{-1}}$, respectively; in contrast, the respective sizes of Pd particles are 1.4, 3.3 and 5.0 nm, from the rough estimation $\mathrm{d}p(\mathrm{nm}) = 1/D$. On PdCHT05, with very small size of metal particles, the condensation of MO with acetone is predominant over hydrogenation. As a result IPHO and TMCO are obtained as the final products via 1,6-intramolecular Michael addition of PHO on basic sites. When the size of Pd particles increases (PdCHT1 and PdCHT2) the hydrogenation of the C=C bond of MO becomes faster than the condensation of MO with acetone. However, deep hydrogenation of C=O bonds to alcohols is still prevented. The loss of selectivity on PdCHT2 occurs at high conversion by the condensation of MIBK with acetone to yield DIBK, or the self-condensation of MIBK to C_{9+}. It comes out that for a similar extent of Pd surface the activity of Pd atoms for hydrogenating the C=C bond in MO increases with the particle size in the range 1–5 nm, but this increase is much larger for hydrogenating C=O bonds in the saturated ketones, acetone and MIBK. This difference of sensitivity towards hydrogenation of C=C and C=O bonds on Pd particles with increasing particle size can be explained in the light of structure–activity relationship in catalysis by metals [20]. It has long been proved that the activity of one surface metal atom for the hydrogenation of unsaturated bonds and hydrogenolysis of saturated bonds may be deeply altered by the size of metal particles [21], the metal–support interaction [22] and the “bimetallic” or “alloying” effect [23]. According to Boudart [24] it means that C=O bond hydrogenation is much more structure-sensitive than that of C=C bond. On that account, one can postulate that there is an optimum size of Pd particle for which the hydrogenation of the C=C bond in MO is fast enough on the one hand, while the hydrogenation of C=O bonds in saturated ketones still remains slow on the other hand. This size might be estimated at ca. 3–5 nm.

4. Conclusions

Pd/Mg(Al)O catalysts with basic, acid and hydrogenating properties are active and selective in the "one-pot" synthesis of methyl isobutyl ketone from acetone and hydrogen. The use of Pd acetylacetonate in H_2O-free toluene solution, for the deposition of Pd on Mg(Al)O, allowed us to keep the basic function properly constant in the various samples. On that account, the changes of catalytic properties can be interpreted mainly by modifications of the metallic function. It is found that the highest selectivity to methyl isobutyl ketone 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 the one hand, and a topology of metallic sites which favors hydrogenation of C═C bond at the cost of C═O bonds on the other hand.

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