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One-Pot Hydroacetylation of Menadione (Vitamin K_3) to Menadiol Diacetate (Vitamin K_4) by Heterogeneous Catalysis

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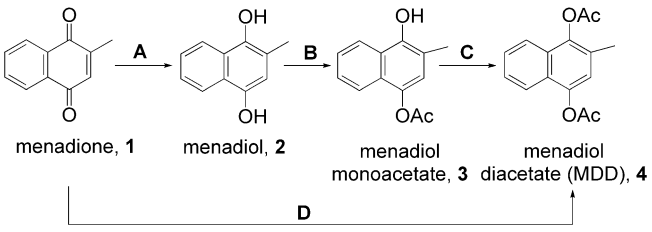
Abstract: Vitamin K_4 (menadiol diacetate, MDD) can be easily synthesized through cleaner and more efficient catalytic alternatives following the green chemistry principles. Ionic gold-based hydroxylated fluorides are active bi-functional catalysts for the one-pot hydroacetylation of menadione leading to MDD with 77% selectivity. Unprecedent results were obtained in the presence of oxide-fluoride catalysts by using a microwave-assisted hydrogen-transfer (Meerwein–Ponndorf–Verley reaction) coupled with an acetylation approach, yielding very high selectivities for the target product (95%).

Keywords: hydroxylated fluorides; ionic gold catalyst; microwaves; oxide-fluorides; vitamin k_4

The term "vitamin K" is used as the generic name for 2-methyl-1,4-naphthoquinone as well as for all derivatives that qualitatively exhibit the same biological activity as phylloquinone (vitamin K_1) in the control of blood clotting.[1] Among all forms of vitamin K, vitamin K_4 (menadiol diacetate, MDD) is the most stable and thus easiest to store. Owing to these qualities, it is a significant candidate as a synthetic substitute for natural vitamins K although its biological activity is 2–3 times lower.[2] The conventional synthesis of MDD consists of three separate consecutive steps: reduction of menadione (**1**) to menadiol (**2**) (Scheme 1, path **A**), monoacetylation of menadiol (**2**) to menadiol monoacetate (**3**) (Scheme 1, path **B**) and monoacetylation of menadiol monoacetate (**3**) to menadiol diacetate (MDD, **4**) (Scheme 1, path **C**).



Scheme 1. The synthesis of MDD (**4**) by separate consecutive steps (paths **A**, **B** and **C**) *versus* direct hydroacetylation (path **D**).

Unfortunately, as in many other cases from the fine chemicals and pharmaceuticals sector the synthesis of these compounds is still based on stoichiometric reactions in the field of organic chemistry where often large amounts of waste are formed, even though cleaner alternatives have been reported. Therefore, the reduction of menadione (**1**) to menadiol (**2**) (Scheme 1, path **A**) is still preferably employed by using inorganic reduction reagents such as sodium dithionite ($Na_2S_2O_4$)[3–5] or Zn-$ZnCl_2$-EtOH reagent[6] while reports upon the catalytic hydrogenation of menadione (**1**) are scarce and not sufficiently detailed.[7,8] On the other hand, menadiol diacetate (**4**) is usually synthesized by using acetic anhydride, in the presence of triethylamine and 4-(dimethylamino)pyridine (DMAP).[4] Such methodologies can not only generate high amounts of inorganic wastes but also raise the price of MDD and decrease its output.

More recently, Raghavender Rao and co-workers[9] stated that menadiol triacetate may be obtained *via* the Thiele–Winter reaction using bismuth(III) triflate as a highly efficient catalyst. However, the use of ho-

mogeneous catalysts does not overcome the known disadvantages connected to the catalysts separation.

Increasingly stringent environmental legislation from the last years has generated a pressing need for cleaner methods of fine chemicals and pharmaceuticals production.[10,11] One of the best solutions is the substitution of classical stoichiometric methodologies by cleaner heterogeneous catalytic alternatives.

Connected with this, Shmachkova and co-workers[12] reported about an attractive one-pot catalytic hydroacetylation of menadione to MDD (Scheme 1, path **D**) in the presence of a bifunctional Pd-based catalyst in which Pd itself catalyzes the menadione hydrogenation to menadiol and the carrier catalyzes the acetylation reactions. Unfortunately, information about the catalyst's nature (i.e., amount of palladium, type of carrier, method of catalyst preparation) and the reaction conditions are unavailable, the method being in this case unusable.

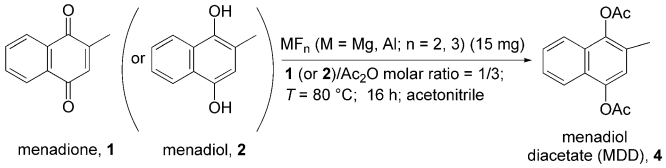
Based on the great interest in cleaner catalytic syntheses of fine chemicals and pharmaceutical intermediates, we took up the challenge task to find and develop a cleaner and efficient alternative for the synthesis of MDD following some of the green chemistry principles such as catalyst usage, replacement of multi-steps synthesis with a one-pot methodology and use of alternative green activation methods for the reactant molecules. Such conversions eliminate the recovery of intermediates and the presence of a catalyst minimizes the need for stoichiometric amounts of reagents, thereby reducing the waste generated.

Herein, we report the key results obtained in the one-pot synthesis of menadiol diacetate (MDD, vitamin K_4) using three different kinds of heterogeneous catalysts: (i) nanoscopic acidic hydroxylated metal fluorides [$MF_{n-x}(OH)_x$, where M = Mg, Al; $n = 2$, 3; $x < 0.1$], (ii) ionic gold-based hydroxylated metal fluorides [$Au^{3+}/MF_{n-x}(OH)_x$], and (iii) magnesium oxide fluorides [$Mg(O)_{(n-x)/2}F_x$] as well as thermal and microwave methods for activation of the reactants.

Nanoscopic acidic hydroxylated metal fluorides [$MF_{n-x}(OH)_x$, in the following named MF_n for simplicity], for which the acidic properties (Lewis/Brønsted) can be easily tuned, have already demonstrated efficiency and versatility in the synthesis of other vitamins (vitamin E, vitamin K_1 and K_1-chromanol).[13,14] They were further tested for the one-pot hydroacetylation of menadione (**1**) to MDD (**4**) (Scheme 1, path **D**) and the results are summarized in Table 1.

As Table 1 shows, these materials (named as MgF_2 and AlF_3) are completely non-active for the one-pot hydroacetylation of menadione to MDD (Scheme 1, path **D**). In contrast, in the presence of the same hydroxylated metal fluorides, the acetylation of menadiol (**2**) [obtained *via* the stoichiometric reduction of menadione (**1**)] occured with conversions (X%) of 84–89% and selectivities (S%) to MDD (**4**) of

Table 1. Catalytic performances of the nanoscopic partly hydroxylated fluorides in the acetylation of menadione or menadiol to MDD **4**.



Catalyst	$X_{menadione}$ [%]	$X_{menadiol}$ [%]	S**2** [%]	S**3** [%]	S**4** [%]
AlF_3-57[a]	0	–	0	0	0
AlF_3-57[b]	–	88.9	–	0.6	99.4
MgF_2-71[a]	0	–	0	0	0
MgF_2-71[b]	–	84.4	–	0	> 99.9

[a] Menadione.
[b] Menadiol.

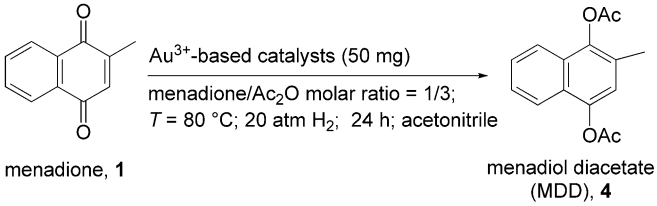
> 99.0%. Obviously, the acetylation of menadione requires a much stronger acidity, which may be provided by catalysts like homogeneous bismuth triflate[9] and not by the nanoscopic acidic hydroxylated metal fluorides – characterized by a medium acidity.[15]

Therefore, with the aim of a one-pot hydroacetylation alternative in mind we have focused on a bifunctional catalyst (i.e., one exhibiting both hydrogenation and acidic functions). Taking into account that the nanoscopic acidic hydroxylated metal fluorides proved to be highly efficient for the acetylation of menadiol to MDD, we prepared a series of bifunctional Au^{3+}/MgF_2 (or AlF_3) catalysts using an easy and facile incipient wetness impregnation method following a reported procedure.[16] Materials with 1 wt% and 4 wt% Au were obtained in this way. The catalytic precursors were calcined at 100 and 150 °C, respectively. The obtained materials were denoted as AuxMg(Al)-y (x = wt% Au; y = calcination temperature). For comparison, the same active species were deposited on carriers with a very soft acidity such as SiO_2.

Noteworthy, the deposition of gold on metal fluorides enabled, indeed, the one-pot hydroacetylation of menadione (**1**) (Scheme 1, path **D**) to diacetylated menadiol (**4**, MDD) while the deposition of gold on silica enabled only the hydrogenation of menadione (**1**) to menadiol (**2**) (Table 2, entries 1 and 2). The obtained results, together with the results obtained in the acylation of menadione/menadiol in the presence of nanoscopic fluorides indicate that, as it was expected, the one-pot synthesis of vitamin K_4 needs a bifunctional catalyst with a hydrogenation function for the menadiol formation (Scheme 1, path **A**) and an acidic one for the acylation step (Scheme 1, paths **B** and **C**).

Unfortunately, the rate of the menadiol acetylation (Scheme 1, paths **B** and **C**) is considerably slower in

Table 2. Catalytic performances of the gold-based catalysts in the one-pot hydroacetylation of menadione **1** to MDD **4**.[a]



Catalyst	$X_{menadione}$ [%]	S**2** [%]	S**3** [%]	S**4** [%]
Au1Si	10.8	99.5	0.5	0
Au4Si	32.6	99.3	0.7	0
Au1Mg-100	11.7	8.7	91.3	0
Au4Mg-100	37.2	11.5	86.0	2.5
Au4Mg-100[a]	57.1	10.8	67.5	21.7
Au4Mg-100[b]	71.3	9.7	47.2	43.1
Au4Mg-100[c]	> 99.9	8.5	14.5	77.0
Au4Mg-150	1.6	0	> 99.9	0
Au4Al-100	33.6	12.0	77.6	10.4

[a] The second catalytic charge.
[b] The third catalytic charge.
[c] The fourth catalytic charge.

comparison those with with pure hydroxylated metal fluorides and this can be assigned to the partial coverage of its surface by gold. This behavior gives a clear indication on the fact that, during the gold species impregnation, part of the active sites for the menadiol acetylation are blocked. This effect is higher for Au4Mg-100 than for Au4Al-100 (Table 2, entries 4 and 9).

Recently, we reported that several reactions including the hydrogenation of isopulegol to menthol occur preferentially on Au^{3+} active species.[16] The electrochemical studies of the prepared fluorides-based catalysts provided evidence that gold exists in all samples as both Au^{3+} and Au^{+} species and that the ratios of these species depend on the catalyst composition and activation procedure (Table 3).

As Table 3 shows, the highest amount of Au^{3+} was found for the Au4Mg-100 sample (Table 3, entry 2). Changing the nature of the fluoride support from MgF_2 to AlF_3 has less influence on the final composition of the catalysts, the amount of Au^{3+} species being almost unchanged (Table 3, entry 4). By increasing the treatment temperature from 100 °C to 150 °C, a large fraction of Au^{3+} becomes reduced to Au^{+} or even metallic species (Table 3, entries 2 and 3). Data compiled in Table 2 show that the conversion of menadione strongly depends on the content of Au^{3+} which depends, in its turn, on the amount of gold and the activation temperature of the catalyst (Table 3) while the selectivity to MDD (**4**) depends on the carrier's acidity (Table 2). Thus, the samples Au4Mg-100 and Au4Al-100 that are characterized by the highest loading of Au^{3+} (Table 3, entries 2 and 4) led to conversions higher than 35% (Table 2, entries 6 and 8). In contrast, the Au4Mg-150 sample with the lowest loading of Au^{3+} (Table 3, entry 3) is almost non active (Table 2, entry 8).

Table 3. Peak currents and the cathodic peak current to anodic peak current ratio for the investigated catalysts.

Catalyst	First scan direction		$-I_{pc}/I_{pa}$
	positive I_{pa} [A]	negative I_{pc} [A]	
Au1Mg-100	5.169×10^{-6}	-5.698×10^{-5}	11
Au4Mg-100	1.119×10^{-5}	-2.621×10^{-4}	23
Au4Mg-150	6.849×10^{-6}	-2.755×10^{-5}	4
Au4Al-100	3.674×10^{-6}	-7.669×10^{-5}	20

Furthermore, the Au^{3+} species are quite rapidly consumed in this reaction, which was further confirmed by cyclic voltammetry experiments (see the Supporting Information). It is again very important to note that a simple separation of the catalyst by filtration, followed by drying the catalyst in air at room temperature for 24 h, led to an enhancement of the conversion of menadione to menadiol up to a level of > 99.9% (Table 2, entries 5–7). Such a behavior is the result of restoring the Au^{3+} oxidation state by a simple contact with air, as it has been confirmed previously by *in situ* XPS experiments.[17] However, the maximum selectivity to MDD (**4**) reached after four catalyst recycling was 77.0% (Table 2, entry 7).

The change of the chemical state of gold with the treatment temperature was also shown by the 'white line' (WL) of the Au L_3-edge absorption spectra (see the Supporting Information). In addition, the XRD patterns show the formation of agglomerated gold particles for the Au4Mg-150 sample with preservation of the amorphous state of the pure nanoscopic fluoride (see the Supporting Information). Therefore, all used techniques display that upon increasing the treatment temperature a decrease of the Au^{3+} species occurs due to the formation of Au^{+} or even metallic Au(0) species. This statement correlated well with the catalytic results showing once again that Au^{3+} are the active sites for the hydrogenation of menadione to menadiol in the one-pot synthesis of MDD (**4**).

Another envisagable solution for the one-pot synthesis of MDD (**4**) is the Meerwein–Ponndorf–Verley (MPV) reduction (which until now has been less studied in the field of heterogeneous catalysis)[18–21] coupled with an acetylation reaction. This method could have the advantage of being more effective due to the fact that MPV is recognized as being very selective for the reduction of C=O bonds.[22]

Using this approach and the above gold-based catalysts resulted in unsatisfactory catalytic performance (e.g., on Au4Mg-100 catalyst, for example, the conver-

sion was 54.6% and selectivity to MDD was 12.1%, respectively). Moreover, the reaction took place only in the presence of NaOH as an external strong base. On the other side, the presence of this strong Brønsted base makes the aldol condensation reaction predominant[23] that is detrimental for the MDD (**4**) selectivity.

The literature information[23–28] concerning the synergetic effect of Lewis basicity and acidity may argue for the new metal oxide fluorides catalysts that have been recently developed in our laboratories[29] for the one-pot hydroacetylation of menadione.

Moreover, the acylation of alcohols and phenols was proven to take place on either basic (e.g., tertiary phosphines, aminophosphine superbase) or acidic [e.g., $ZnCl_2$, $Sc(OTf)_3$, 1,3-disubstituted tetraalkyldistannoxanes] catalysts.[30–34]

These oxide fluorides possess acid-base sites as there are Lewis acid sites (undercoordinated Mg^{2+}), Brønsted base sites (OH groups) and Lewis base sites (negatively charged oxide) in different proportions and different strengths, which depends on the F^-/OH^- ratio.[29]

For this purpose we prepared a series of magnesium oxide fluoride (MgF_xO_y) samples (with $x=1.9$–0.1 and $y=0.05$-0.95), in which the basicity increases with the amount of oxygen while the acidity increases with the amount of fluoride (see the Supporting Information).[29] In this way, the Lewis acid sites of $MgF_{1.9}O_{0.05}$ are stronger than those of $MgF_{0.1}O_{0.95}$ while both the OH groups and the basic oxygen sites on $MgF_{0.1}O_{0.95}$ are more strongely basic than those on the other sample (see the Supporting Information). Apparently, in the MPV reaction in the presence of acid-base catalysts, 2-propanol is adsorbed at the dual acid-base sites which causes its dissociation into the corresponding alkoxide, and the ketone at the adjacent acidic and basic sites before the hydrogen-transfer reaction takes place.[24] The isopropoxide formed from 2-propanol transfers a hydride ion that attacks the carbon atom in the carbonyl group.[27] It is thus expected that a solid catalyst with a proper ratio and strength of the acid/base sites, regardless of the material type, should be an efficient catalyst for the MPV reduction.

An initial screening of the obtained oxide fluorides showed rather low conversions ($<12\%$) for a reaction time of 48 h. But the reaction rate was significantly increased by using a microwave-assisted hydroacylation approach. Under these conditions, for the samples with a fluoride content lower than 0.8, the reaction time was shorted from 48 h to 3 h and a high selectivity to MDD was obtained. The selectivities also achieved high levels. While on $MgF_{0.2}O_{0.9}$, a sample that possesses mild acidity and strong basicity, a high selectivity to MDD of 95% resulted for a 40% conversion of menadione, on $MgF_{0.4}O_{0.8,}$ characterized by a stronger acidity and a milder basicity than the former, the selectivity to MDD was 84.0% for a conversion of menadione of 22.8%.

These results suggest that this reaction requires a synergetic effect of strong basicity and mild acidity and oxide fluorides are among the best candidates which are able to generate such an effect.[26,27] Moreover, under these reaction conditions the acid-base surface sites of the catalysts also enable acetylation of the menadiol obtained in the initial hydrogen-transfer step.

In conclusion, we can state that the partly hydroxylated MgF_2 materials are too soft acidic materials to promote the acetylation of the very stable menadione molecule, but strong enough for the acetylation of menadiol. The impregnation of these materials with gold salts transforms them into active and selective bi-functional catalysts for the one-pot hydroacetylation of menadione to MDD. An even higher activity in combination with a higher selectivity to the target product was obtained in the presence of acid-basic metal oxide fluoride materials using a microwave-assisted hydrogen-transfer (MPV reaction) coupled with an acetylation approach. Thus, working under microwave-assisted MPV–hydroacetylation an unprecedented high activity and selectivity to MDD ($X=40\%$, $S=95\%$) was obtained on the $MgF_{0.2}O_{0.9}$ catalyst. As it was mentioned above, the catalytic performances of this sample are assigned to a synergetic effect of strong Lewis basicity and mild acidity. Therefore, we strongly believe that these promising catalysts can also be applied for other reactions that need such combinations.

Experimental Section

Menadione (97 wt%) was purchased from Across Organics.

Synthesis of Menadiol (2)

To a suspension of menadione (2-methylnaphthoquinone, 50 g, 290 mmol) in AcOEt (400 mL) a solution of $Na_2S_2O_4$ (100 g, 574 mmol) in water (400 mL) was added at room temperature. The resulting mixture was stirred for 0.5 h at the same temperature. The organic layer was separated, washed with water (2×200 mL), and concentrated under reduced pressure. The residue was triturated with *n*-hexane (300 mL) and the resulting crystals were collected by filtration, washed with *n*-hexane (100 mL), and dried under reduced pressure to give menadiol as a pale purple crystalline powder (procedure in agree with Tomimatsu[3]). ^{1}H NMR (DMSO-d_6): $\delta=2.23$ (s, 3H), 6.58 (s, 1H), 7.29–7.36 (m, 2H), 7.95–8.01 (m, 2H), 8.22 (s, 1H), 9.33 (s, 1H).

Catalytic Synthesis of Menadiol Diacetate (Vitamin K_4, 4)

Catalytic acetylation of menadiol: In a typical procedure, 174 mg (1 mmol) of menadiol (MDL) were dissolved in

4 mL of acetonitrile in a glass vial with a standard capacity of 8 mL, equipped with a magnetic stirrer. To this mixture 306 mg (3 mmol) acetic anhydride (menadiol/Ac_2O molar ratio = 1/3) and 15 mg of hydroxylated fluoride (MgF_2 or AlF_3) were added. After sealing the vial, it was immersed in an oil bath at 80 °C, and the reaction mixture was stirred at 1500 rpm for 16 h.

Catalytic hydroacetylation of menadione with molecular hydrogen and thermal conditions: In a typical procedure, 172 mg (1 mmol) of menadione were dissolved in 4 mL of acetonitrile in a stainless steel autoclave of 25 mL capacity. To this mixture 306 mg (3 mmol) acetic anhydride (menadione/Ac_2O molar ratio = 1/3) and 50 mg of gold-based fluoride catalyst were added. After sealing the autoclave, 20 atm of H_2 were introduced. Under autoclave conditions the stirring rate was 1200 rpm, reaction temperature of 80 °C and reaction time 24 h. For a new catalytic charge, the gold-based catalyst was separated from the reaction mixture by filtration, dried in air, at room temperature, and reintroduced for another 24 h in the same reaction mixture, under identical reaction conditions.

Catalytic hydroacetylation of menadione in MPV conditions (thermal conditions): 172 mg (1 mmol) of menadione were dissolved in 6 mL of an isopropyl alcohol/acetic anhydride (1/1) mixture in a glass vial with a standard capacity of 10 mL, equipped with a magnetic stirrer. To this mixture 50 mg of catalyst (e.g., gold-based fluoride or oxidefluoride) were added. After sealing the vial, it was immersed in an oil bath at 80–110 °C, and the reaction mixture was stirred at 1500 rpm for 22 h. When gold-based catalysts were used, some tests in the same conditions but in the presence of NaOH were also made.

Catalytic hydroacetylation of menadione in MPV conditions and under microwave irradiation: Microwave-assisted reactions were carried out with a Milestone Start S system operating at 600 W. The stirring rate inside the reactor was 350 rpm. Typical experiments were carried out using 172 mg (1 mmol) of menadione, 408 mg (4 mmol) of Ac_2O (menadione/Ac_2O molar ratio = 1/4), 15 mL of acetonitrile and 2 mL of isopropyl alcohol. To this system 50 mg of catalyst (oxide fluoride) were added and the slurry was maintained at 80–140 °C, under stirring, for between 1 and 4 h.

The temperature inside the vessel was controlled using either a thermocouple (thermal conditions) or a fiber optic (microwave irradiations). Irrespective of the applied methodology, after the reaction was stopped, the catalyst was separated by filtration and the liquid phase was removed under vacuum at 80 °C. The obtained product was then dissolved again in acetonitrile and analyzed by chromatography.

Menadiol monoacetate (intermediate 3) ^{1}H NMR (DMSO-d_6): δ = 2.38 (s, 3H), 2.43 (s, 3H), 7.03–7.09 (m, 2H), 7.42–7.46 (m, 1H), 7.6 (s, 1H), 7.62 (m. 1H), 7.88–7.90 (m, 1H).

Menadiol diacetate (vitamin K_4) ^{1}H NMR (DMSO-d_6): δ = 2.38 (s, 3H), 2.40 (s, 3H), 2.54 (s, 3H), 7.21–7.90 (m, 5H).

Irrespective of the reaction procedure, the reaction product was analyzed through GC [Shimadzu instrument with FID detection, capillary WCOT Fused Silica CP-Wax 58 (FFAP) CB column of 50 m length] and characterized by GC-MS (ThermoElectron Corporation DSQ) and ^{1}H, ^{13}C NMR spectroscopy (Bruker AV 400 spectrometer, in DMSO-d_6 as solvent and Me_4Si as internal standard).

Synthesis of Magnesium Oxide Fluorides

50 mL of dry methanol were added to 1.56 g of magnesium metal (Aldrich, 99.98%) in a round-bottom flask with a reflux condenser for 3 h. An understoichiometric amount of HF (n_1 = 102 mmol for $MgF_{1.6}O_{0.2}$ and n_2 = 26 mmol for $MgF_{0.4}O_{0.8}$) dissolved in MeOH was added to the obtained $Mg(OCH_3)_2$ solution. After adding to this solution the necessary amount of distilled water (V_1 = 1 mL; n = 52 mmol and V_2 = 3.7 mL; n = 207 mmol, respectively) and aging for 12 h, the final gels were dried under vacuum at T = 70 °C for 5 h. The dry powder obtained in this way was calcined in Ar for 3 h at 350 °C

Electrochemical Studies on the Prepared Ionic Gold-based Fluoride Catalysts

Commercially available reagents were used without further treatment: carbon powder (Aldrich, o.d. = 1–2 mm), paraffin oil (Sigma–Aldrich, 0.827–0.890 g·cm^{-3}), sulfuric acid (Merck, 95–97wt%, p.a., d = 1.84 g cm^{-3}), and tetrachloroauric(III) acid purum (Sigma–Aldrich, 50% Au basis, d = 3.9 g cm^{-3} at 25 °C).

Measurements were performed on working electrodes [i.e., CPE (carbon paste electrode) (Au^{3+}/Au^{+}) modified with ionic gold electroactive species originating from catalysts prepared from a very fine powder of gold-based hydroxylated fluorides (e.g., Au1Mg-100, Au4Mg-100, Au4Mg-150, Au4 Al-100) mixed with carbon paste (CP) and paraffin oil in 1.25:2.5:1.0 wt. ratio]. A copper wire was used for electrical contacts. Before each measurement, the surface of the modified electrode was prepared by the following steps: rinsed with distilled water, polished, rinsed again with distilled water, dried in air, and polished once again until a mirror-like surface was obtained.

Electrochemical studies were performed with an electrochemical workstation (Autolab 12, Eco-Chemie, Utrecht, Netherlands) coupled to a PC running the GPES software to allow experimental control and data acquisition. The three electrodes system consisted of the modified electrode [CPE (Au^{3+}/Au^{+})] as working electrode, Ag/AgCl,KCl (3 M) as reference electrode, and a platinum wire as counter electrode. All potentials are referred to Ag/AgCl,KCl (3 M). As electrolyte solution was used either 0.2 N sulfuric acid or 0.2 N hydrochloric acid. Prior to each measurement the solution was degassed for 5 min with extra-pure argon gas and an inert atmosphere was maintained by purging argon at low pressure above the solution.

FT-IR Measurements

The IR experiment was carried out using a Perkin–Elmer S 2000 with a spectral resolution of 4 cm^{-1}. The sample was pressed into a self-supported wafer with an area weight of 15 mg/cm^2. The wafer was placed in a stainless steel, low temperature infrared cell with CaF_2 windows. The sample was activated in the IR cell under vacuum at different temperatures for 24 h. After activation the sample was cooled using liquid N_2 in the presence of an inert gas (He, 2 mbar) to 77 K. The CO pressure was increased stepwise. The spec-

tra are shown as difference of the spectrum of the sample in the presence of CO minus the spectrum of the sample before CO dosage. The magnesium oxide fluorides were again treated under vacuum at 573 K for 2 h. After reactivation the sample was treated with stepwise increasing pressures of CO_2.

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