

Photoassisted Catalytic Oxidation of Carbon Monoxide at Room Temperature

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Summary. The thermal and photoassisted catalytic oxidation of CO at metal oxide supported $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ was studied at room temperature. Contrary to neat $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ the supported catalysts suffer from fast deactivation attributed to strong adsorption of the reaction product carbon dioxide. The latter can be efficiently removed from the catalyst surface at elevated temperatures. In some cases, *i.e.* for catalysts supported with selected *n*-type semiconductors (TiO_2 , SnO_2 , WO_3), efficient CO_2 desorption and good, constant catalytic activity was observed upon visible light irradiation. Under such conditions the CO to CO_2 conversion observed for $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{TiO}_2$ was nearly as good and stable as for the unsupported catalyst. It is suggested that light absorption promotes carbon dioxide desorption through positive charging of the catalyst surface.

Keywords. CO oxidation; Photocatalysis; Ruthenium dioxide; Oxides; Semiconducting supports.

Introduction

The catalytic air oxidation of carbon monoxide at room temperature is a reaction of general importance for a variety of basic and applied research fields, including safety devices and air purification [1]. One of the best investigated catalyst is crystalline ruthenium dioxide (rutile structure), however the produced CO_2 desorbs from the surface only at elevated temperatures (*ca.* 600 K). The mechanism of this catalytic process as occurring at a single crystal plane was investigated in great experimental and theoretical detail [2–4]. Contrary to this, we found that

amorphous hydrated ruthenium dioxide catalyzes CO oxidation by humid air already at room temperature [5]. Only gold nanoparticles are also known to catalyze this reaction under similar mild conditions [6–8].

Hydrous ruthenium dioxide has attracted attention due to its special catalytic and electronic properties. It is a good proton and electron conductor with abilities for efficient charge storage [9, 10]. Its activity in CO oxidation at room temperature remains nearly unchanged within several catalytic cycles. At higher temperatures the catalyst loses water and becomes less active or inactive. High concentrations of CO induce a vigorous reaction accompanied by overheating and deactivation of the catalyst if not efficiently cooled. Activation energies of 36.0 kJ mol^{-1} were calculated from temperature dependence in the range of 22–79°C [5]. Since ruthenium dioxide is a rather expensive material, we tested whether supporting onto inorganic oxides may afford catalysts requiring less amounts of ruthenium. Furthermore, the support may act as a heat sink and influence the reaction mechanism. In addition to thermal CO oxidation also photooxidation was investigated.

Results and Discussion

Preparation of Catalysts

Hydrous ruthenium dioxide is a black, amorphous powder exhibiting only two broad peaks in the XRD spectrum at 2θ of *ca.* 33 and 55° (spectrum not

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shown). A high specific surface area of $104 \text{ m}^2 \text{ g}^{-1}$ is obtained from *BET* measurements. The pressed $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ material shows a good electric conductivity in agreement with literature data [9, 11]. After grinding ruthenium dioxide hydrate with TiO_2 (P25, Degussa) the specific surface area of this new material (30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ /P25) was only $58 \text{ m}^2 \text{ g}^{-1}$, *i.e.* close to the value characteristic for P25 (*ca.* $50 \text{ m}^2 \text{ g}^{-1}$). Unless otherwise noted, the supported materials were prepared by grinding the two powders in a mortar. The resulting powders were black.

Catalytic Activity in the Dark and Under Irradiation

$\text{RuO}_2 \cdot x\text{H}_2\text{O}$ synthesized according to the procedure described previously [5] shows a relatively good and stable activity (Fig. 1). It is, however, much less

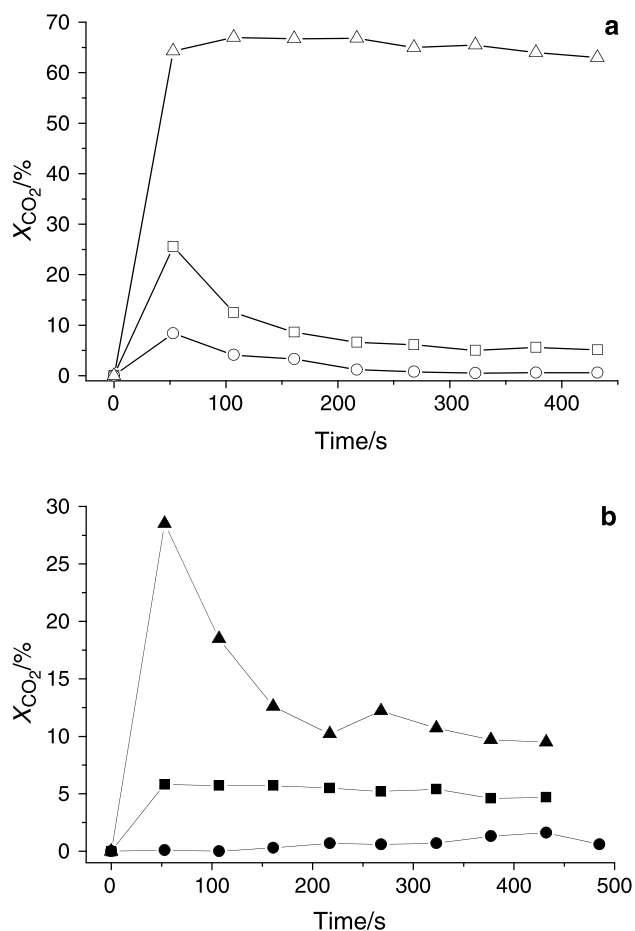


Fig. 1. Influence of salt and acid adsorption on catalytic activity. (a) $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (Δ) and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ impregnated with NaCl (\square), NaHSO_4 (\circ). (b) $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ exposed to HCl gas for 90 min (\blacksquare) and 16 h (\bullet), after 16 h exposition followed by heating for 2 h at 150°C (\blacktriangle) (see text). RT, 1% CO/O_2

active when the precipitate formed during oxidative hydrolysis from ruthenium(III) chloride is not washed carefully. In order to check the influence of H^+ , Cl^- , and other ions on the catalytic properties, the catalysts $\text{NaCl}/\text{RuO}_2 \cdot x\text{H}_2\text{O}$, $\text{NaHSO}_4/\text{RuO}_2 \cdot x\text{H}_2\text{O}$, and $\text{HCl}/\text{RuO}_2 \cdot x\text{H}_2\text{O}$ were prepared. In the first two cases the appropriate salt was used for impregnation of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ in aqueous suspension, while in the third case $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ was exposed to vapour of concentrated HCl. In all cases conversion of CO to CO_2 decreased significantly as compared to unmodified $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (Fig. 1), most likely by blocking active sites of the catalyst. In the case of $\text{HCl}/\text{RuO}_2 \cdot x\text{H}_2\text{O}$ it was possible to recover the activity of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ through HCl desorption by heating the $\text{HCl}/\text{RuO}_2 \cdot x\text{H}_2\text{O}$ material to $90\text{--}150^\circ\text{C}$. However, after reaching a maximum activity the conversion rate decreased rapidly (Fig. 1b). This is in accord with the much lower activity of dehydrated ruthenium dioxide [5].

The activity of various supported $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ materials towards CO oxidation is compared in Fig. 2. In the case of neat $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ a constant CO conversion factor of 65% was reached at room temperature under our experimental conditions, which can be considered as a reference value. This factor increased to 78% when the catalyst was irradiated with visible light ($400 \text{ nm} < \lambda < 650 \text{ nm}$). All sup-

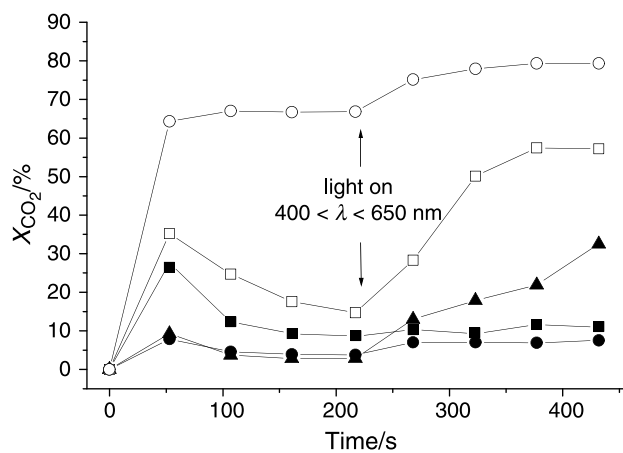


Fig. 2. Time dependence of CO conversion factor for various catalysts prepared by grinding the metal oxide with 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. Unsupported $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (\circ), 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{Fe}_2\text{O}_3$ (\square), 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{WO}_3$ (\bullet), 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{SnO}_2$ (\blacktriangle), RT, 1% CO/O_2 . During first 220 seconds of each test the catalysts were kept in the dark; afterwards they were illuminated with visible light (220 s)

ports were inactive (within 1–2% conversion) both in the dark or under irradiation.

Activities of the supported materials in the dark follow a general behavior: after a relatively high conversion factor observed within the first minute of the reaction, further CO oxidation slows down significantly (*vide infra*). The resulting deactivated catalysts can be reactivated by purging them with a stream of oxygen at room temperature or slightly elevated temperatures affording catalysts of almost same activities as compared to the original materials. However, the maximum conversion factors of 35, 26, and 10% measured for TiO₂ (P25), Fe₂O₃, and SnO₂ or WO₃ supported catalysts indicate a decrease in catalytic activity as compared to unsupported ruthenium dioxide hydrate.

When irradiation with visible light was employed, in some cases the conversion factors increased again to reach a higher, nearly constant level. The best results, both in the dark and upon illumination, were observed for the materials with a semiconductor as the support. In the case of 30% RuO₂·xH₂O/P25 the conversion factor reached a constant level at 55%, which is much higher than the values of 30, 13, and 10% observed for SnO₂, Fe₂O₃, and WO₃ supported materials.

Figure 3 summarizes CO oxidation at RuO₂·xH₂O supported by three different ways onto pyrogenic SiO₂ (Degussa, Aerosil 200, specific surface

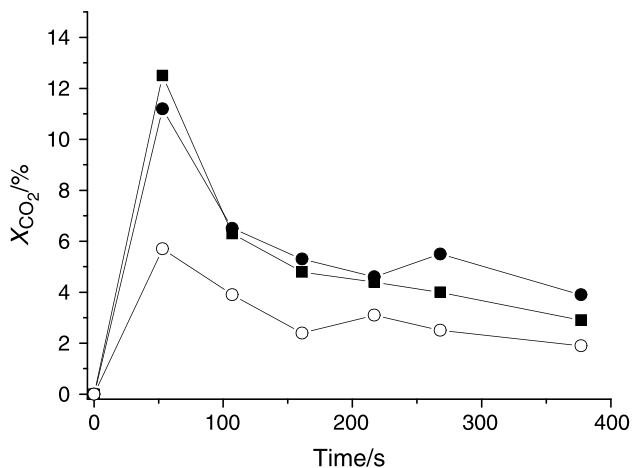


Fig. 3. Catalytic activity of 10% RuO₂·xH₂O/Aerosil 200 prepared by grinding Aerosil 200 with RuO₂·xH₂O, (●) and (■) before and after thermal treatment, respectively (see text), and of 20% RuO₂·xH₂O/Aerosil 200 prepared by impregnation of Aerosil 200 with RuCl₃ followed by hydrolysis. RT, 1% CO/O₂

area of 200 m² g⁻¹). The first material was prepared by grinding both components together, the second was additionally heated at 75°C for *ca.* 20 h and then for 1.5 h at 200°C. Both catalysts were gray and exhibited low conversion factors of 11 and 13%, respectively. The third material was prepared by impregnation of Aerosil 200 with RuCl₃·xH₂O followed by a standard oxidative hydrolysis and heating at 150°C for 24 h. This catalyst was only half as active as the two other ones. These results and other tests with SiO₂ as a support clearly revealed that pyrogenic silica induces a strong decrease of catalytic activity, although it has a large surface area. Apparently, the activity decreases with increasing interaction between RuO₂·xH₂O and SiO₂ as concluded from the comparison of ground and impregnated RuO₂·xH₂O/Aerosil 200 catalysts. The latter procedure should induce formation of Si–O–Ru bonds, analogous to those observed in preparations of silica supported cadmium sulfide [12].

Since RuO₂·xH₂O on the titania powder P25, which is a mixture of 70% anatase and 30% rutile, exhibited the highest activity among the supported catalysts, a mutual influence of the nature of titania crystal modification was investigated. 30% RuO₂·xH₂O/P25, 30% RuO₂·xH₂O/TH (anatase), and 30% RuO₂·xH₂O/rutile were prepared by grinding an appropriate amount of the support with RuO₂·xH₂O. Surprisingly, the conversion factor for the TH and rutile based catalysts was only 15%, *i.e.* one third of the value for the P25 supported material (Fig. 4). This further demonstrates, as already mentioned

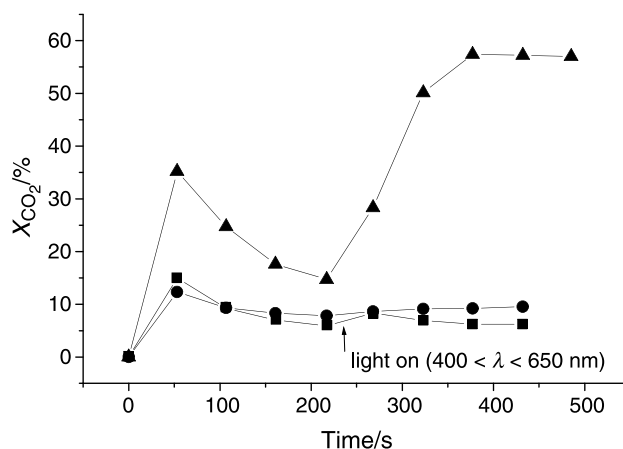


Fig. 4. Influence of titania crystal modification on catalytic activity of various 30% RuO₂·xH₂O/TiO₂ materials prepared by grinding: rutile (■), TH (anatase) (●), P25 (70% anatase, 30% rutile) (▲). RT, 1% CO/O₂

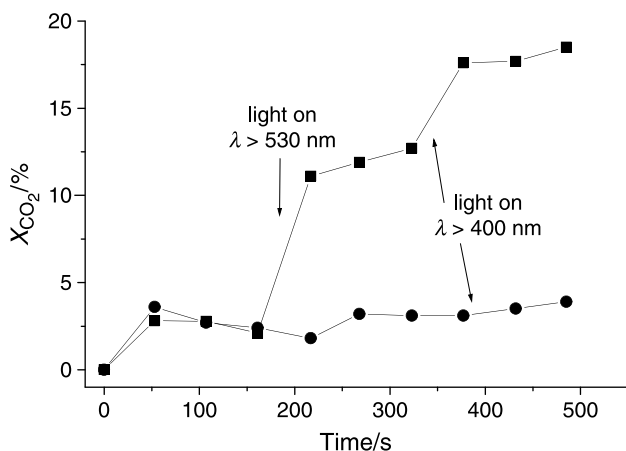


Fig. 5. Influence of the semiconductor type on catalytic activity of 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{SiC}$ materials prepared by grinding *n*- (■) and *p*-type (●) silicon carbide. RT, 1% CO/O_2

above, that the specific surface of the support does not determine the catalytic activity since rutile has a value of *ca.* $3 \text{ m}^2 \text{ g}^{-1}$ whereas $330 \text{ m}^2 \text{ g}^{-1}$ were measured for TH. The beneficial role of irradiation is very significant in the case of 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$ whereas it is nearly negligible for the two other samples.

To find out whether the nature of the majority carriers of the semiconductor may have an influence on the catalytic activity, *n*- and *p*-type silicon carbide were used as supports. Whereas in the dark both 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/n\text{-SiC}$ and 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/p\text{-SiC}$ exhibited about the same low conversion factor of 3%, only the *n*-SiC based catalyst showed a strong photoeffect, irrespective if excited at $\lambda > 530 \text{ nm}$, a wavelength where only ruthenium dioxide absorbs light, or at $\lambda > 400 \text{ nm}$, where also the support can absorb (Fig. 5). Although this result suggests that an electron transfer from $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ to the supporting semiconductor takes place upon irradiation, no visible light induced photocurrent ($400 \text{ nm} < \lambda < 600 \text{ nm}$) was detectable in photoelectrochemical measurements with 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$, 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/n\text{-SiC}$, and 20% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{SiO}_2$ based ITO electrodes.

CO₂ Adsorption and Desorption

Maier *et al.* [13] reported that the deactivation of many CO oxidation catalysts is caused mainly by product inhibition. Reactivation can be performed by purging with N_2 , O_2 or air at temperatures between 50 and 100°C . Under such conditions adsorbed carbon dioxide is efficiently desorbed. We assumed,

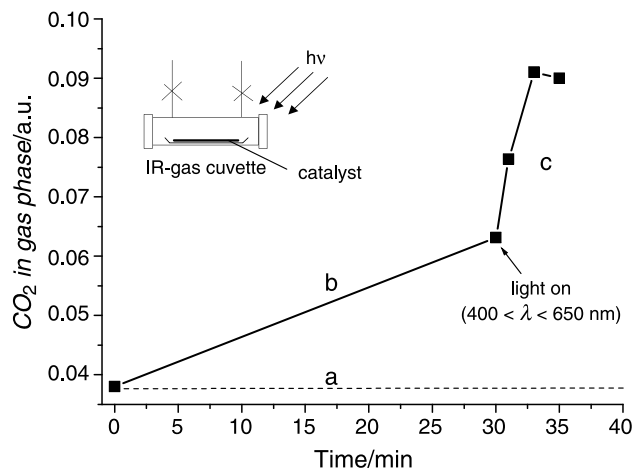


Fig. 6. Thermal and photochemical desorption of CO_2 from 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$ (RT); a) initial CO_2 concentration, b) thermal desorption, c) photodesorption

that CO_2 desorption from the surface of 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$ may be enhanced upon irradiation with visible light. In order to test this assumption, the catalyst was first purged with a stream of CO_2 for 15 min. Then it was transferred into the IR gas-cuvette filled with N_2 and appearance of CO_2 in the gas phase was followed by IR spectroscopy (Fig. 6). Whereas a rather slow CO_2 desorption occurred in the dark, it became much faster upon irradiation with visible light. To exclude that this effect arises from local heating, irradiations generally were performed through filters which removed UV and IR light. Since the absorption spectra of the supports do not extend into the visible, light can be absorbed only by the black $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ component.

From the results presented above it follows that in all cases supporting of ruthenium dioxide hydrate onto a metal oxide carrier reduces the thermal catalytic activity as compared to the unsupported catalyst. The reduction is about 50% in the case of TiO_2 and 64–86% in the case of SnO_2 and $\text{Fe}_2\text{O}_3/\text{WO}_3$, respectively. Furthermore, the conversion factors pass through a maximum with increasing reaction time whereas they reach a constant plateau when the support is absent (Fig. 1). If the reaction is conducted under irradiation with light which can be absorbed only by the ruthenium catalyst, the strongest enhancement is observed when titania, a typical *n*-type semiconductor, is the support. Together with the observation, that *n*-type SiC exhibited a stronger photoeffect than *p*-type SiC, these observations suggest that an electron injection from excited ruthenium

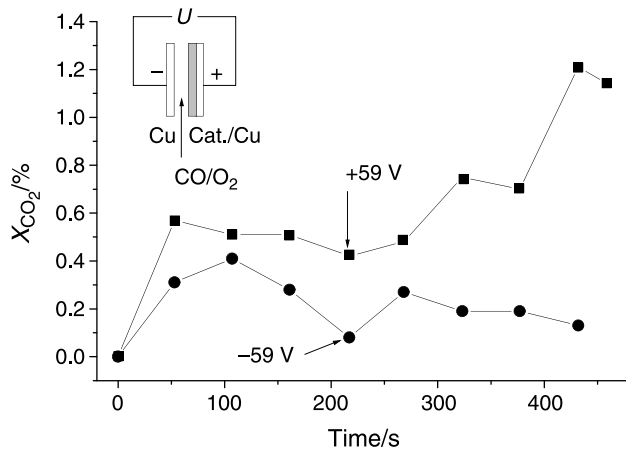


Fig. 7. Influence of the sign of applied voltage on the 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$ catalysed reaction; RT, 1% CO/O_2 , capacitor-type reactor

nium dioxide into the semiconductor may occur. The resulting positive charge at the catalyst should increase the acidity of the hydrated ruthenium dioxide surface and therefore favor desorption of carbon dioxide. To obtain experimental evidence for the proposed positive charging, 30% $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{P25}$ was placed onto one copper plate of a capacitor through which the mixture of CO/O_2 was passed. It turned out that application of a positive voltage to this plate induced a more efficient thermal CO oxidation as compared to applying no or a negative charge (Fig. 7). Although this result clearly suggests that the photoenhancement of the conversion factor is due to a positive catalyst charging, a very small beneficial contribution of photoinduced local heating cannot completely be ruled out.

Experimental

$\text{RuO}_2 \cdot x\text{H}_2\text{O}$ was prepared by oxidative hydrolysis of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as previously described [5]. The resulting material was dried at 60°C . Supported catalysts have been prepared analogously but in the presence of commercially available oxides or by grinding the support with the corresponding amounts of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. The oxides SiO_2 , Fe_2O_3 , SnO_2 , WO_3 were used as received. The following titania powders were employed: P25 (Degussa, ca. 70% anatase + 30% rutile, $50\text{ m}^2\text{ g}^{-1}$), TH (KerrMcGee, anatase, $330\text{ m}^2\text{ g}^{-1}$), rutile (Aldrich, $3\text{ m}^2\text{ g}^{-1}$). The $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ content in the material is always given in wt%. *n*-SiC and *p*-SiC were obtained from Prof. A. Winnacker, University of Erlangen-Nürnberg.

In a typical experiment of CO oxidation the gas mixture (1 vol% CO in O_2) was pumped through the catalyst bed (25 mg of catalyst powder spread on cotton wool). The transparent reactor made of glass enabled irradiation ($400\text{ nm} <$

$\lambda < 650\text{ nm}$) of the catalyst with a halogen lamp (150 W, Osram) through an IR water filter and two cut-off filters. The gas mixture was passing through an IR gas cuvette (10 cm optical path) with KBr windows.

The CO and CO_2 contents were analyzed with a Perkin Elmer 16 PC FT-IR spectrometer and XRD spectra were collected at a Philips X'Pert PW 3040/60 instrument. Conversion factors X_{CO_2} were calculated from IR absorption of CO ($2100\text{--}2200\text{ cm}^{-1}$) and CO_2 ($2300\text{--}2400\text{ cm}^{-1}$) within $\pm 5\%$ uncertainty. Specific surface areas have been determined with a Gemini 2370 apparatus according to BET theory. Diffuse reflectance spectra of the solids were recorded on a Shimadzu UV-2401PC UV/Vis scanning spectrophotometer equipped with a diffuse reflectance accessory.

A three-electrode set-up was employed for photoelectrochemical measurements. The electrolyte solution was 0.1 M NaOH. Solutions were bubbled with nitrogen for 10 min prior to measurement. Platinum and Ag/AgCl were used as auxiliary and reference electrodes. Working electrodes were prepared by casting a suspension of the appropriate material in water onto ITO-glass plates (Präzisions Glas) and drying in air. Thereby a porous film was formed which allowed the electrolyte to penetrate into the bulk of the electrode. A 1000 W Xe-lamp (XBO, Osram) in a Mueller housing equipped with a water filter was used for irradiation. The working electrodes were irradiated from the backside (through the ITO-glass) in order to minimize the influence of thickness of the catalyst layer on the photocurrent. A Metrospec monochromator (AMKO) was applied to choose the appropriate energy of radiation. The photoelectrochemical measurements (current vs. potential upon irradiation, current vs. irradiation wavelength at constant potential) were controlled by a BAS Epsilon potentiostat.

The pellets of selected materials were prepared in a typical press used for preparation of KBr pellets. The pellet was attached to a copper plate of a capacitor, which played the role of the reactor. The distance between the pellet and the second copper plate was approximately 1 mm. A dc voltage of ca. 60 V was applied to the capacitor during the reaction run.

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