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Gas-phase selective oxidation of cyclohexanol to cyclohexanone over Au/Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ catalysts: On the role of Cu doping

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The industrial production of cyclohexanone from cyclohexanol would benefit from a selective oxidation catalyst. Herein, Cu doping of MgCr$_2$O$_4$ supports for gold nanoparticles active in gas-phase oxidation of cyclohexanol was investigated. Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ exhibited spinel structures (x $<$ 0.25: MgCr$_2$O$_4$; x = 1: CuCr$_2$O$_4$) onto which 3–4 nm gold nanoparticles could be dispersed. Cu doping led to higher activity. During reaction, surface Cu$^{2+}$ was reduced to Cu$^0$, resulting in Au–Cu alloy formation. At low temperature, low-Cu-content catalysts (x $<$ 0.1) showed higher activity than high-Cu-content catalysts, likely because the Au–Cu alloy with highly diluted Cu was more active for the dehydrogenation step of cyclohexanol. However, Au/Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Au/Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ showed lower cyclohexanol conversion at high temperature than samples with high Cu content, because O$_2$ activation involving Cu becomes rate-limiting. Stable cyclohexanol conversion and cyclohexanone selectivity were 99.1% and 90.2% (space-time yield of 266 gKetone gAu$^{-1}$ h$^{-1}$) for Au/Mg$_{0.5}$Cu$_{0.5}$Cr$_2$O$_4$ at 300 °C.

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1. Introduction

Cyclohexanone is an important intermediate compound in the production of nylon. In the chemical industry, cyclohexanone is obtained through direct dehydrogenation of cyclohexanol using Zn- or Cu-based catalysts [1–9]. However, cyclohexanol dehydrogenation process is limited by thermodynamic equilibrium under practical conditions. Moreover, catalysts used for this process deactivate gradually as heavy side-products block the active sites [10–12]. Thus, frequent regeneration is required. In contrast, oxidative dehydrogenation of cyclohexanol does not suffer from equilibrium limitations. The use of an oxidant can furthermore significantly suppress the formation of carbonaceous deposits. Thus, the development of a highly active and selective catalyst for oxidative dehydrogenation is desirable.

Supported gold nanoparticle (AuNP) catalysts have attracted substantial interest in the field of heterogeneous catalysis for the oxidation of alcohols due to their exceptional catalytic properties [13–19]. However, the number of studies dealing with catalytic oxidation of cyclohexanol using gold catalysts is limited. Liquid-phase oxidation of cyclohexanol with high selectivity toward cyclohexanone has been reported using gold supported on Cu-Mg-Al [20] and Ga-Al [21] mixed oxides. The use of solvents and catalyst separation remain critical issues in liquid-phase processes. Li et al. studied the selective oxidation of cyclohexanol in the gas phase using AuNPs confined in ordered mesoporous silica. The catalysts showed good selectivity and stability, but the activity was relatively low [22]. Zhao et al. reported the application of a microstructured Au/Ni-fiber catalyst for the same process, requiring relatively high temperature for achieving a reasonable cyclohexanol conversion [23]. Clearly, more efforts are required to design highly active and selective gold catalysts for the gas-phase conversion of cyclohexanol to cyclohexanone.

For supported gold catalysts, their catalytic performance is strongly dependent on the size of AuNPs and the strength of the gold-support interaction [24–26]. Generally, the size of gold nanoparticles should be controlled below 5 nm to achieve good catalytic performance. This can be achieved by suitable gold-support interaction. Another role of the support is to participate in the catalytic reaction, in particular at the gold-support interface. For instance, as gold does not effectively activate molecular oxygen, the use of a suitable support for oxygen activation is indispensable for preparing active and selective oxidation catalysts. [27–31]. For oxygen activation, metal oxides such as TiO$_2$ [32–34] and CeO$_2$ [35–38] are often used. Oxygen vacancies on these reducible supports can strongly adsorb and activate molecular oxygen [39–42].
Spinel oxides with the general chemical formula \( AB_2O_4 \) (\( A = M^{2+}, B = M^{3+} \)) are another interesting class of stable oxides, whose redox properties can be tuned by using redox-active trans-mlents in their structure [43–45]. In a recent work, we reported that a copper-doped \( \text{MgCr}_2\text{O}_4 \) spinel oxide (\( \text{MgCuCr}_2\text{O}_4 \)) can disperse and stabilize \( \sim 3 \) nm AuNPs. The resulting catalysts showed good catalytic performance in the gas-phase oxidation of cyclohexanol to cyclohexanone [46].

It was demonstrated that copper in a spinel with the \( \text{Mg}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{O}_4 \) composition provided high activity and selectivity, and the Au–Cu synergy at the gold-support interface was suggested to play an important role in the oxidation reaction. In the present work, we study in more detail the role of Cu in these selective oxidation catalysts. Specifically, we are interested in the influence of Cu doping on the physico-chemical, structural and catalytic properties of the final gold catalysts. Based on these investigations, deeper insights into the Au–Cu synergy is derived and the Cu content is optimized with respect to catalytic performance in oxidative dehydrogenation of cyclohexanol.

2. Experimental

2.1. Catalyst preparation

Spinel oxides with the general formula \( \text{Mg}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4 \) (\( x = 0, 0.01, 0.1, 0.25, 0.5, 0.75, 1 \)) were prepared by a coprecipitation-calcination method using metal nitrates as precursors. As an example, we prepared \( \text{Mg}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{O}_4 \) by adding 400 ml of a \( \text{NaOH} \) aqueous solution (1 M) dropwise to 250 ml of a mixed nitrate solution containing \( \text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (37.10 mmol), \( \text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} \) (12.37 mmol), and \( \text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) (37.10 mmol). The base amount was chosen such that all metal ions precipitate. After stirring for 20 h, the obtained slurry was filtered, washed and dried at 110 °C overnight, followed by calcination at 700 °C for 8 h at a rate of 2 °C/min in air.

Gold was deposited on the spinel oxide support via a deposition-precipitation method (DPU) using urea as the precipitating agent as developed by Louis and co-workers [47]. Typically, 2.0 g of \( \text{Mg}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4 \) spinel oxide and 0.6 g urea were added to a 100 ml flask, to which 67 ml of \( \text{HAuCl}_4 \) (1.5 mmol/L) was added. Afterwards, the mixture was stirred and heated to 90 °C in an oil bath and kept at this temperature for 20 h under reflux. Then, the mixture was cooled to room temperature and washed with deionized water. Finally, the solid was dried at 60 °C overnight and calcined at 300 °C for 4 h at a rate of 2 °C/min in air. The as-prepared gold catalysts are denoted as \( \text{Au/}\text{Mg}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4 \). The targeted gold loading is 1.0 wt%.

2.2. Catalyst characterization

Nitrogen physisorption was carried out on a Tristar 3000 automated gas absorption system. The samples were degassed at 120 °C overnight before analysis. The Au loading was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after extraction of gold in aqua regia.

X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phase powder diffraction system using Cu Kα radiation. Scanning electron microscope (SEM) was carried out using a FEI Quanta 200F scanning electron microscope. Transmission electron microscopy (TEM) micrographs were acquired on a FEI Tecnai 20 electron microscope at an acceleration voltage of 200 kV with a LaB6 filament. The average gold particle size was determined by measuring the size of at least 200 gold particles. The element distribution of the gold catalysts was studied using scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy (STEM-EDX). Measurements were carried out on a FEI cubed Cs-corrected Titan operating at 300 kV. Samples were sonicated in ethanol and dispersed on a holey Al support grid. Elemental analysis was done with an Oxford Instruments EDX detector X-MaxN 100TLE.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo Scientific K-Alpha spectrometer, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 72 W and a spot size of 400 μm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2 × 10⁻⁸ mbar and during measurement 3 × 10⁻⁶ mbar Ar because of the charge compensation dual beam source. Data analysis was performed using the CasaXPS software. The binding energies were corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.6 eV.

Temperature-programmed reduction experiments (\( \text{H}_2\)–TPR) were performed in a Micromeritics Autochem II 2920 equipped with a fixed-bed reactor, a computer-controlled oven, and a thermal conductivity detector. Typically, 100 mg catalyst was loaded in a tubular quartz reactor. The sample was reduced in 4 vol% \( \text{H}_2/\text{N}_2 \) at a flow rate of 10 ml/min, while heating from room temperature to 800 °C at a rate of 5 °C/min.

2.3. Catalytic activity measurements

Gas-phase oxidative dehydrogenation of cyclohexanol to cyclohexanone was carried out using a fixed bed plug flow reactor. Typically, 100 mg of catalyst (125–250 μm) diluted with 400 mg SiC was loaded into a stainless-steel reactor with an internal diameter of 8 mm. Prior to reaction, the catalyst was pretreated in \( \text{He} \) for 4 h at 260 °C. Then, the reaction mixture with the volumetric composition \( \text{alcohol/O}_2/\text{He} = 1/6/133 \) was introduced into the reactor at a flow rate of 168 ml/min (corresponding to a space velocity of around 100,000 ml\text{g}^{-1}\text{h}^{-1}) at 260 °C. Cyclohexanol was fed to the system by a HPLC pump and all the lines were kept at ca. 130 °C to avoid condensation of the reactants and products. When the reaction reached a steady state after the observed induction period, the catalytic performance of the various Au/\( \text{Mg}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4 \) catalysts was then tested at different reaction temperatures from 200 °C to 300 °C. The effluent gas was analyzed by an online gas chromatography equipped with a TCD and a FID. The conversion of cyclohexanol (\( X \)) and selectivity to cyclohexanone (\( S \)) were determined in the following manner:

\[
X(\%) = \frac{\text{total } C \text{ mol} \times 6 \times \text{cyclohexanol mol}\%}{\text{total } C \text{ mol}\%} \times 100
\]

\[
S(\%) = \frac{6 \times \text{cyclohexanone mol}\%}{\text{total } C \text{ mol} \times 6 \times \text{cyclohexanol mol}\%} \times 100
\]

3. Results and discussion

We first studied the influence of Cu doping content on the crystal phase of spinel oxides. Fig. 1 depicts the XRD patterns
of the catalysts after loading the support with gold followed by calcination. The patterns of the supported gold catalysts are similar to these of the parent spinel oxides (see Fig. S1), although some samples contain diffraction peaks due to gold nanoparticles. At low Cu doping level (x ≤ 0.25), the supports exhibit the same spinel structure as MgCr$_2$O$_4$ (JCPDS 10-0351, pirochlore). An increase of the Cu doping level leads to changes of the diffraction patterns as can be seen for Mg$_{0.5}$Cu$_{0.5}$Cr$_2$O$_4$ and Mg$_{0.25}$Cu$_{0.75}$Cr$_2$O$_4$. The phase changes towards that of CuCr$_2$O$_4$ spinel (JCPDS 34-0424), which is also the structure of our CuCr$_2$O$_4$ sample at x = 1. In order to highlight the possible formation of AuNPs, the XRD patterns are shown in a magnified way in the 20 = 36.5–39.5° region (Fig. 1). Only a very weak diffraction feature at 20 = 38.2° could be observed, which corresponds to the (1 1 1) plane of Au. Thus, the XRD patterns indicate that gold is highly dispersed on the prepared spinel oxides. SEM images of the as-prepared Au/Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ samples are shown in Fig. S2. The gold loading amount and the surface areas as determined by ICP element analysis and nitrogen physisorption, respectively, are summarized in Table 1. The gold loading is close to the targeted value of 1.0 wt% for all catalysts, indicative of the high deposition efficiency of the DPU method. Au/MgCr$_2$O$_4$ has the largest surface area (24.6 m$^2$/g) of all the gold catalysts. Cu doping of the spinel oxide leads to decreasing surface area, the smallest surface area (3.8 m$^2$/g) was obtained on Au/Mg$_{0.25}$Cu$_{0.75}$Cr$_2$O$_4$.

H$_2$-TPR was conducted to study the reducibility of the spinel-supported gold catalysts. As shown in Fig. 2, the Au/MgCr$_2$O$_4$ sample did not show reduction features, in line with our previous result (41). All other Cu-containing samples showed a reduction feature, except for the one with the lowest Cu content (Au/Mg$_{0.99}$Cu$_{0.01}$Cr$_2$O$_4$), which is probably due to the very low Cu content. A small reduction feature at ca. 750 °C is observed for Au/Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$. Au/Mg$_{0.75}$Cu$_{0.25}$Cr$_2$O$_4$ displayed a small reduction feature at much lower temperature (ca. 200 °C) and a main one at 650 °C, which we attribute respectively to the reduction of copper species in the surface and in the bulk of the spinel oxides. A further increase of the Cu content led to more complex TPR profiles, with the main reduction peak shifting to lower temperature, indicating that copper species are more easily reduced at higher Cu doping content.

We used TEM to determine the gold particle size and size distribution of the as-prepared Au/Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ catalysts. The results in Fig. 3 show that AuNPs are well dispersed on the spinel oxide supports, in accordance with the XRD data, with a relatively narrow size distribution. Au/MgCr$_2$O$_4$ contained the largest AuNPs with an average size of 3.9 nm. The average AuNP size for the Cu-containing samples was around 3 nm, among which

| Table 1 | Physicochemical properties of the fresh Au/Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ catalysts. |
|---------|-----------------|-----------------|-----------------|-----------------|
| Sample  | [Au] (wt%)$^*$  | S$_{BET}$ (m$^2$/g) | D$_{Au}$ (nm)$^b$ | D$_{Au}$ (nm)$^c$ |
| Au/MgCr$_2$O$_4$ | 1.01 | 24.6 | 3.9 | 4.0 |
| Au/Mg$_{0.99}$Cu$_{0.01}$Cr$_2$O$_4$ | 1.05 | 8.5 | 3.0 | 3.4 |
| Au/Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ | 1.00 | 10.6 | 2.8 | 3.2 |
| Au/Mg$_{0.75}$Cu$_{0.25}$Cr$_2$O$_4$ | 1.02 | 10.3 | 2.9 | 3.3 |
| Au/Mg$_{0.5}$Cu$_{0.5}$Cr$_2$O$_4$ | 1.09 | 6.2 | 3.8 | 4.1 |
| Au/Mg$_{0.25}$Cu$_{0.75}$Cr$_2$O$_4$ | 1.08 | 3.8 | 3.2 | 3.6 |
| Au/CuCr$_2$O$_4$ | 1.02 | 6.9 | 3.5 | 3.8 |

$^*$ Determined by ICP-OES. $^b$ Average AuNP size of fresh catalysts, determined by TEM. $^c$ Used catalysts, determined by TEM.
Au/Mg0.5Cu0.5Cr2O4 presented a slightly larger gold particle size (3.8 nm). We next studied the catalytic performance of the Au/Mg1-xCuCr2O4 catalysts in the gas-phase oxidation of cyclohexanol to cyclohexanone.

Fig. 4 shows the activity of the spinel-supported gold catalysts in the gas-phase oxidation of cyclohexanol at 260 °C. Au/MgCr2O4 displayed a relatively low cyclohexanol conversion (16%), which was nearly constant in the first 10 h. In contrast, Cu doping enhanced the activity significantly. The highest initial activity was observed for the sample with the lowest Cu content (Au/Mg0.99Cu0.01Cr2O4). The Cu-containing gold samples show an increasing activity with time on stream during which cyclohexanol conversion increased gradually in the first 30 h followed by a steady state. After attaining a steady state, we further evaluated the catalytic performance at temperatures between 200 °C and 300 °C, as shown in Fig. 5. Some interesting activity trends can be found in Fig. 5a. In the low-temperature regime, Au/Mg0.99-CuCr2O4 exhibited the highest activity at 200 °C (X = 28.9%). An increase of the Cu doping content led to a lower cyclohexanol conversion (X = 6.3% for Au/CuCr2O4 at 200 °C). On the other hand,
in the high-temperature regime, the gold catalysts with higher Cu content were more active than the low-Cu-content ones. For instance, Au/Mg0.25Cu0.75Cr2O4 gave the highest cyclohexanol conversion (98.7%) at 300 °C. While this catalyst showed a strong increase in the conversion with temperature, the conversion rise
was less pronounced for Au/Mg0.99Cu0.01Cr2O4 and Au/Mg0.25Cu0.75Cr2O4, whose cyclohexanol conversion increased slowly to 88.1% and 85.9% at 300 °C, respectively.

In the gas-phase oxidation of cyclohexanol, cyclohexanone is the desired reaction product, with cyclohexenone and COx being the side products (Scheme 1). Fig. 5b–d shows the selectivity to these products for the Au/Mg0.99Cu0.01Cr2O4 catalysts. The selectivity toward cyclohexanone was close to 100% at low temperature for all the gold catalysts and decreased to ca. 90% at high temperature. Au/Mg0.9Cu0.1Cr2O4 and Au/Mg0.25Cu0.75Cr2O4 showed higher selectivity to cyclohexanone at 300 °C (5.8% and 6.7%, respectively) in comparison to the high-Cu-content catalysts, whose selectivity toward COx was higher at 300 °C. The selectivity to COx was 9.7% and 7.4% for Au/Mg0.5Cu0.5Cr2O4 and Au/Mg0.25Cu0.75Cr2O4, respectively.

The activity of the spinel oxides without gold was also measured in the oxidation of cyclohexanol (Fig. S3). Without gold these spinel oxides are nearly inactive for the reaction. Furthermore, the catalytic test in the absence of O2 revealed that O2 is necessary for the selective oxidation reaction (Fig. S4).

To study the stability of the spinel-supported catalysts, we evaluated the activity of Au/Mg0.99Cu0.01Cr2O4 and Au/Mg0.25Cu0.75Cr2O4 during consecutive heating and cooling, as shown in Fig. S5. No deactivation was observed during the cooling branch for these two catalysts. Thus, we can exclude the possibility that Au/Mg0.99Cu0.01Cr2O4 suffered from deactivation at high temperature as a cause for the relatively low activity at 300 °C. As Au/Mg0.25Cu0.75Cr2O4 displayed the highest activity in the reaction at 300 °C, its long-term catalytic stability was evaluated as well (Fig. 6). An activation period was observed in the first 30 h and then a steady state was attained at 260 °C, where the cyclohexanol conversion and the selectivity to cyclohexanone reached 74.4% and 98.2%, respectively. An increase of the reaction temperature to 300 °C led to a cyclohexanol conversion of 99.1%, while the selectivity toward cyclohexanone decreased to 90.2% (selectivity toward COx and cyclohexanone 7.4% and 2.4%, respectively). The space-time yield of cyclohexanone reached 266 g gcat⁻¹ h⁻¹. No obvious deactivation was observed in the following 50 h, indicating that Au/Mg0.25Cu0.75Cr2O4 was very active and stable at 300 °C.

To explore the origin of the observed activity trends for the spinel-supported gold catalysts, we further characterized the used catalysts. Fig. 7 shows the gold particle size and size distribution of the gold catalysts after the reaction. The AuNP size increased only slightly after reaction compared to the fresh ones, indicating that no severe sintering occurred during the reaction. This result explains the good catalytic stability of the Au/Mg1-xCu0Cr2O4 catalysts.

We used XPS to study the Au and Cu oxidation states on the as-prepared and used catalysts. Fig. S6 shows the corresponding Au 4f XP spectra. As the Mg 2 s signal overlaps with the Au 4f5/2 component, the Au 4f7/2 was used for quantitative analysis. Its position at around 84 eV suggests that gold was in the metallic state in the as-prepared and used samples. Fig. 8a–f shows the relevant Cu 2p3/2 XP spectra. Two peaks are discerned at 934.3 eV and 931.8 eV. The higher binding energy (B.E.) peak is attributed to Cu2+ in the spinel oxides, while the lower B.E. peak is assigned to Cu0 or Cu+ species [48–53]. Furthermore, the shake-up satellite peak characteristic of Cu2+ can also be observed in the 938–945 eV region. The amount of Cu2+ was decreased after the reaction due to the reduction of Cu species to lower oxidation states. This occurred for all Cu-containing samples. As analysis of the Cu 2p region cannot distinguish Cu0 from Cu+ species, we also measured the Cu LMM Auger spectra (Fig. 8g–l). Cu+ has a lower Auger electron kinetic energy at around 916.8 eV than Cu0 and Cu2+, which have similar kinetic energies at around 918 eV [49,53]. When the Cu content was very low (Au/Mg0.99Cu0.01Cr2O4), the Cu LMM signal was too weak to be discerned. For the other Cu-doped catalysts, a peak at ca. 917.8 eV can be observed. There is no obvious shift observed for this peak on the used catalysts, indicating that Cu0 is the main reduced Cu species instead of Cu+.

The surface atomic composition of the used Au/Mg1-xCu0Cr2O4 catalysts is shown in Table 2 and Table 3. The surface gold content is the highest on Au/Mg0.25Cu0.75Cr2O4. We explain this by the higher amount of gold nanoparticles per unit surface area on this sample due to the low support surface area. The surface Cu0 content increased with Cu content in the catalysts (see Table 3).

As it is well known that metallic Au and Cu can form alloys, we surmised that a Au–Cu alloy might be formed during the catalytic reaction. We selected three samples with different Cu content, i.e., Au/Mg0.9Cu0.1Cr2O4, Au/Mg0.75Cu0.25Cr2O4, Au/Mg0.25Cu0.75Cr2O4 for more detailed electron microscopy involving HAADF-STEM and EDX mapping. The STEM-EDX maps of the as-prepared catalysts in Fig. S7 show that Mg, Cu, and Cr are well distributed in the spinel oxides with gold nanoparticles on their surface. The STEM-EDX maps of the three used catalysts are shown in Figs. 9–11. Clearly, a Au–Cu alloy formed during the selective oxidation reaction. EDX provides an estimate of the elemental composition of the alloy particles, which decreased in terms of Au/Cu ratio from 3.8 for Au/Mg0.9Cu0.1Cr2O4 to 1.9 for Au/Mg0.25Cu0.75Cr2O4. This result is in line with the higher Cu0 content of the Cu-rich samples as determined by XPS (Table 3). Based on the STEM-EDX analysis, we confirm that the reduced Cu0 species migrated from the spinel oxide support to the gold nanoparticles and formed Au–Cu alloy particles. Accordingly, we infer that the induction period during the catalytic reaction observed in Fig. 4 is related to alloy formation. This is schematically shown in Scheme 2. Additionally, the composition of the Au–Cu alloy was also influenced by the Cu doping content in the spinel oxide, where a more Cu-rich alloy was formed at a higher Cu doping level of the support.
O 1s XP spectra were measured to study the different oxygen species on the surface of the as-prepared and used gold catalysts. In the spectra shown in Fig. 12, three peaks can be observed at 529.9 eV, 531.7 eV, and 533.3 eV, which can be assigned to lattice oxygen (O\textsubscript{a}), oxygen adsorbed on oxygen vacancy (O\textsubscript{b}), and surface-adsorbed H\textsubscript{2}O (O\textsubscript{c}) \cite{54–58}, respectively. Table 4 shows the relative contributions of the three surface oxygen species. The O\textsubscript{b}/O\textsubscript{a} ratio increased considerably for the used Au/Mg\textsubscript{1–x}Cu\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} catalysts compared to the as-prepared ones at \( x \geq 0.25 \). This increase is less pronounced for the low-Cu-content catalysts with \( x \leq 0.1 \). This is reasonable, because the catalyst surface was reduced during the catalytic reaction (Fig. 8).

Moreover, we can expect that more oxygen vacancies are formed when the surface contains more Cu. It is also clear that the used samples with higher Cu content (\( x \geq 0.25 \)) have a higher O\textsubscript{b}/O\textsubscript{a} ratio (ca. 0.9) than the two catalysts with lower Cu content (\( x \leq 0.1 \)), leading to values smaller than 0.5. We infer from these differences that there are more oxygen vacancies present on the Au/Mg\textsubscript{1–x}Cu\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} catalysts (\( x \geq 0.25 \)) after reaction than on those with lower Cu content (\( x \leq 0.1 \)).

Next, we discuss the origin of the catalytic behavior observed on the Au/Mg\textsubscript{1–x}Cu\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} catalysts at low and high temperature (Fig. 5a). In the oxidation of cyclohexanol to cyclohexanone, both cyclohexanol and O\textsubscript{2} should be activated to achieve a complete...
Table 2
Surface atomic composition of used Au/Mg1-xCuxCr2O4 catalysts as determined by XPS.

| Sample       | Au(%) | Mg(%) | Cu(%) | Cr(%) | O(%)  |
|--------------|-------|-------|-------|-------|-------|
| Au/MgCr2O4   | 0.3   | 6.3   | –     | 18.2  | 75.2  |
| Au/Mg0.9Cu0.1Cr2O4 | 0.8 | 6.7   | 0.3   | 18.6  | 73.6  |
| Au/Mg0.75Cu0.25Cr2O4 | 1.0 | 3.9   | 0.7   | 17.3  | 77.1  |
| Au/Mg0.25Cu0.75Cr2O4 | 1.9 | 3.9   | 0.7   | 17.3  | 77.1  |
| Au/CuCr2O4   | 0.9   | –     | 8.5   | 14.4  | 76.2  |

Table 3
Distribution of Cu oxidation states on the surface of used Au/Mg1-xCuxCr2O4 catalysts as determined by XPS.

| Sample       | Cu(%) | Cu2+(%) | Cu0(%) |
|--------------|-------|--------|--------|
| Au/Mg0.99Cu0.01Cr2O4 | 0.3   | –      | –      |
| Au/Mg0.75Cu0.25Cr2O4 | 1.9   | 0.6    | 1.3    |
| Au/Mg0.5Cu0.5Cr2O4   | 1.9   | 0.6    | 1.3    |
| Au/Mg0.25Cu0.75Cr2O4 | 6.0   | 1.1    | 4.9    |
| Au/CuCr2O4         | 8.5   | 2.5    | 6.0    |

Fig. 8. Cu XPS and Cu LMM spectra of as-prepared and used Au/Mg1-xCuxCr2O4 catalysts.
Fig. 9. STEM-EDX analysis of used Au/Mg_{0.9}Cu_{0.1}Cr_{2}O_{4}.

Fig. 10. STEM-EDX analysis of used Au/Mg_{0.75}Cu_{0.25}Cr_{2}O_{4}.
catalytic cycle. Scheme 2 emphasized the formation of defects (oxygen vacancies) on the support due to the reduction and migration of Cu. On this basis, a possible reaction mechanism is shown in Scheme 3. These oxygen vacancies serve as sites for the activation of molecular O₂ forming active oxygen species. These oxygen species are involved in the activation of O–H bonds in cyclohexanol. C–H bond activation (dehydrogenation) constitutes an elementary step catalyzed by metallic gold. After desorption of cyclohexanone, H₂O is formed and desorbs leading to a new oxygen vacancy. When the reaction temperature was low, Au/Mg₀.₉₉Cu₀.₀₁Cr₂O₄ and Au/Mg₀.₉Cu₀.₁Cr₂O₄ showed higher activity than other catalysts with higher Cu content. Considering the catalytic data and STEM-EDX results, we speculate that the Au–Cu alloy with a lower Cu content at the surface is more active for the dehydrogenation of cyclohexanol than a Au–Cu alloy with a higher Cu surface content. Wrasman et al. reported that the Au–Pd alloy with isolated Pd atoms is the most active catalyst for the selective oxidation of 2-propanol to acetone [59]. We propose a similar effect for the Au–Cu system. On the other hand, when the reaction temperature was high, Au/Mg₀.₉₉Cu₀.₀₁Cr₂O₄ and Au/Mg₀.₉Cu₀.₁Cr₂O₄ could not reach a cyclohexanol conversion as high as observed for the more Cu-rich samples. We speculate that this is due to a lower amount of Cu sites able to activate molecular oxygen. These sites may be located at the nanoparticle-support interface, but it is likely that the Cu species at the surface of the alloyed nanoparticles also contributed to the synergy. Literature mentions SiO₂-supported
Au—Cu alloy catalysts to be active for alcohol oxidation reactions [16,60,61]. Thus, for low-Cu-content catalysts the activation of O\textsubscript{2} might limit the reaction. At high temperature, the metal-catalyzed C—H bond cleavage step is likely not controlling the rate anymore and, instead, the rate appears to correlate with the Cu content, indicating that oxygen activation is likely the rate-determining step in the overall mechanism. Clearly, the oxidation of cyclohexanol requires the involvement of both a metal phase (Au—Cu) and a spinel oxide support. The dehydrogenation step might be the rate-controlling step at low temperature, while the activation of O\textsubscript{2} affected the reaction process more significantly at high temperature.

4. Conclusions

In this work, we have performed a systematic study of the influence of Cu doping on the structural and catalytic properties of Au/Mg\textsubscript{1—x}Cu\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} catalysts in the gas-phase oxidation of cyclohexanol to cyclohexanone. At low Cu content (x ≤ 0.25), the supports had the MgCr\textsubscript{2}O\textsubscript{4} crystal phase, while higher Cu content led to the crystal phase transformation towards CuCr\textsubscript{2}O\textsubscript{4} phase at x > 0.25. AuNPs with an average size of 3–4 nm could be easily dispersed on the spinel oxide supports by a DPU method. Cu doping drastically improved the catalytic performance in the selective oxidation of cyclohexanol. XPS analysis shows that Cu\textsuperscript{2+} was
reduced to Cu° during the catalytic reaction, leading to the formation of a supported Au–Cu alloy with nearly the same particle size as in the as-prepared catalysts. The Cu content of the Au–Cu alloy particles was higher for more Cu-rich Mg1–xCuxCr2O4 supports. In the low temperature regime, low-Cu-content catalysts (x ≤ 0.1) showed higher activity than those with higher Cu doping level (x ≥ 0.25), likely Au–Cu alloy with a lower Cu content is more active for the most difficult C–H bond cleavage step. The different activity trend at higher temperature can be explained by a shift in the rate-limiting step to oxygen activation. Then, the activity correlates to the amount of Cu. An O 1s XPS analysis indicates that surface vacancies of the support are involved, although we cannot exclude that the Cu species in the Au–Cu alloy can also promote oxygen activation. In a 50 h catalytic test, a stable cyclohexanol conversion of 99.1% in combination with a selectivity toward cyclohexanone of 90.2% was obtained (space-time yield = 266 gKetone gAu⁻¹ h⁻¹) for Au/Mg0.25Cu0.75Cr2O4 at 300 °C. This optimized catalyst is promising for the gas-phase selective oxidation of cyclohexanol to cyclohexanone.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.02.025.

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