Identification of Active Sites in the Catalytic Oxidation of 2-Propanol over Co$_{1+x}$Fe$_{2-x}$O$_4$ Spinel Oxides at Solid/Liquid and Solid/Gas Interfaces

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A series of Co$_{1+x}$Fe$_{2-x}$O$_4$ (0 \leq x \leq 2) spinel nanowires was synthesized by nanocasting using SBA-15 silica as hard template, which was characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. The Co$_{1+x}$Fe$_{2-x}$O$_4$ spinels were applied in the aerobic oxidation of aqueous 2-propanol solutions to systematically study the influence of exposed Co and Fe cations on the catalytic properties. The activity of the catalysts was found to depend strongly on the Co content, showing an exponential increase of the reaction rate with increasing Co content. Ensembles of Co$^{3+}$ (coordinatively unsaturated) sites were identified as the active sites for selective 2-propanol oxidation, which are assumed to consist of more than six Co ions. In addition, gas-phase oxidation with and without water vapor co-feeding was performed to achieve a comparison with liquid-phase oxidation kinetics. An apparent activation energy of 94 kJ mol$^{-1}$ was determined for 2-propanol oxidation over Co$_2$O$_3$ in the liquid phase, which is in good agreement with the gas-phase oxidation in the presence of water vapor. In contrast to gas-phase conditions, the catalysts showed high stability and reusability in the aqueous phase with constant conversion in three consecutive runs.

Introduction

Selective oxidation is a key technology in the chemical industry, in particular for the functionalization of hydrocarbons in petrochemistry. The main challenge in catalytic oxidation is the control of selectivity. Industrial processes are typically performed at high temperatures (> 300°C) in the gas phase with partial conversion since total oxidation to CO$_2$ and H$_2$O may occur under these harsh conditions as a consecutive reaction. The participation of lattice oxygen of the catalysts according to the Mars-van Krevelen mechanism is commonly accepted. By comparison, lattice oxygen is expected to be immobile under much milder conditions in the liquid phase. Therefore, the catalytic activity is determined by the mobility and reactivity of adsorbed activated intermediates at the solid-liquid interfaces.

The selective oxidation of alcohols in the liquid phase over noble metal-based catalysts such as supported Au, Pd, Pt, and Ag as well as bimetallic Au–Pd nanoparticles has been extensively investigated in the last decades. Among various alcohols, 2-propanol oxidation is a suitable probe reaction that provides mechanistic information and enables the comparison between gas- and liquid-phase conditions. Three different selective reaction routes can be observed under mild liquid-phase reaction conditions in particular: dehydrogenation [Eq. (1)], oxidative dehydrogenation [Eq. (2)], and dehydration [Eq. (3)] of 2-propanol. At high temperatures, total oxidation of 2-propanol or intermediate species forms CO$_2$ and H$_2$O:

\[
(\text{CH}_3)_2\text{CHOH} \rightarrow (\text{CH}_3)_2\text{CO} + \text{H}_2 \\
2 (\text{CH}_3)_2\text{CHOH} + \text{O}_2 \rightarrow 2 (\text{CH}_3)_2\text{CO} + 2 \text{H}_2\text{O} \\
(\text{CH}_3)_2\text{Cho} \rightarrow \text{CH}_2 = \text{CHCH}_3 + \text{H}_2\text{O} 
\]

Besides the redox activity, acid-base properties are also probed, since dehydration yielding propene takes place at strong acidic or weak basic sites, while the dehydrogenation to acetone requires moderate acidic or strong basic sites. Somorjai and co-workers investigated the 2-propanol oxidation over Pt nanoparticles at the solid/liquid and solid/gas interfaces.
interfaces. They found different kinetics, which they attributed to the different orientations of adsorbed 2-propanol as observed by sum frequency generation (SFG) spectroscopy. Furthermore, water enhanced the reaction rate in the liquid phase, while the rate was decreased in the gas-phase reaction. Bürgi et al. investigated the oxidation of 2-propanol over Pd/Al₂O₃ in the liquid phase and proposed an oxidative dehydrogenation mechanism comprising dissociative adsorption of 2-propanol forming an adsorbed 2-propoxide intermediate followed by dehydrogenation yielding acetone. The α–C–H bond cleavage was found to be the rate-determining step (rds) as indicated by the observation of the 2-propoxide intermediate. Although the knowledge about heterogeneous noble metal catalysis in the liquid phase is continuously growing, their application suffers from high cost and the tendency to poisoning and leaching. Transition metal-based oxides are available at lower cost and have comparably higher stability against poisoning and leaching. Nevertheless, concepts are still lacking relating the interplay of composition, structure, and reactivity over metal oxide catalysts in the liquid phase.

Mixed metal oxides crystallizing in the spinel structure are highly suitable for providing these concepts. Stoichiometric spinels have the general formula of ABO₄ with divalent A²⁺ and trivalent B³⁺ cations. The cations occupy octahedral and tetrahedral sites in the oxygen anion sublattice. In the normal spinel structure such as Co₃O₄, 1/4 of the tetrahedral sites are occupied by A²⁺ ions and 1/2 of the octahedral sites are filled by B³⁺ ions. In an inverse spinel like CoFe₂O₄, the trivalent B³⁺ ions occupy 1/4 of the tetrahedral and 1/2 of the octahedral sites, while divalent A²⁺ ions occupy 1/2 of the octahedral sites. The composition can be varied in a broad range via isomorphous cation exchange, while the crystal structure still remains stable. Thus, spinel structures can be used as model system to explore the catalytic properties of different metal cation substitutions.

Co–Fe-based spinel oxides showed high activity in the catalytic combustion of CO and of volatile organic compounds (VOC) in the gas phase. Haruta and coworkers found a beneficial effect of Fe substitution on the catalytic activity of Co₃O₄ in low-temperature CO oxidation. The temperature corresponding to 50% CO conversion (Tₕ₅₀) decreased from 273 to 188 K by substitution of 15% Fe and remained similar up to 25% Fe. Besides total oxidation, Co–Fe-based spinel catalysts also showed excellent activity in selective oxidation, in particular of 2-propanol in the gas phase. For example, monocristalline CoFe₂O₄ synthesized by thermal decomposition of a layered double hydroxide was very active in dehydration yielding propene, while commercial CoFe₂O₄ primarily catalyzed the oxidative dehydrogenation to acetone. Further, Co₃O₄ selectively catalyzed the oxidative dehydrogenation reaching nearly full conversion with 100% selectivity to acetone at 430 K. Generally, the high activity and selectivity is ascribed to exposed coordinatively unsaturated Co³⁺ species (Co³⁺Cod). Such understanding about the active sites in the liquid phase is still lacking.

In the present study, we systematically investigated the influence of Co and Fe ions in a series of CoₓFe₃–ₓO₄ (0 ≤ x ≤ 2) spinel oxides synthesized by nanocasting on the catalytic activity in 2-propanol oxidation in the aeous phase. The exponential increase of the reaction rate with increasing Co/(Co + Fe) ratio revealed that Co cations are much more active than Fe cations and that Co-containing ensembles with more than six Co cations are the active sites. Kinetic studies over Co₃O₄ were performed to obtain the apparent activation energy as well as the reaction orders of 2-propanol and O₂. Oxidation of 2-propanol in the gas phase was performed with and without water vapor co-feeding over Co₃O₄ and compared with the liquid-phase oxidation to investigate the influence of water and to gain deeper insight in the nature of the active site. In addition, the reusability was examined, and the reaction network was investigated by performing acetone oxidation.

Results and Discussion

Characterization

The obtained mesostructured spinel catalysts were investigated by XRD (Figure 1). All catalysts showed the characteristic

![Figure 1. XRD patterns of the Co–Fe-based spinel catalysts with Co₃O₄ (black, PDF: 00-042-1467) and CoFe₂O₄ (blue, PDF: 00-022-1086) reference patterns.](https://www.chemcatchem.org/cctc/202100352)
The specific surface areas are similar for Co$_{12}$-Fe$_{18}$O$_{48}$ and Co$_{16}$Fe$_{18}$O$_{48}$ ranging between 125 and 137 m$^2$g$^{-1}$, while Co$_{2.62}$Fe$_{3}$O$_{48}$ shows an increased surface area of 178 m$^2$g$^{-1}$ (Table 1). TEM images of pristine Co$_{2.91}$O, Co$_{2.25}$Fe$_{3}$O$_{48}$, and Co$_{2.82}$Fe$_{3}$O$_{48}$ are compared in Figure 2. Highly ordered arrays of nanowires are visible for Co$_{2.82}$Fe$_{3}$O$_{48}$ revealing a perfect replication of the SBA-15 template.

The diameter and pore size of the Co$_{2.82}$Fe$_{3}$O$_{48}$ nanowires are around 8 and 3 nm, respectively, which fit very well to the pore size and the wall thickness of the SBA-15 silica hard template aged at 100°C.[23] For Co$_{2.25}$Fe$_{3}$O$_{48}$ smaller and less ordered domains are obtained which can be attributed to a lower degree of interconnectivity. Even smaller and less ordered domains are obtained with Co$_{2.62}$Fe$_{3}$O$_{48}$ displaying mainly agglomerates of small nanoparticles. The TEM images suggest that Fe$^{3+}$ alters the growth of the nanowires because of the lower thermal decomposition of iron(III) nitrate compared with cobalt (II) nitrate and/or the interaction of Fe$^{3+}$ with the SiO$_2$ template.[24] This is also in agreement with the larger specific area and the smaller crystallite size compared with the samples with higher Co content. Co and Fe ions are evenly distributed as shown by elemental mappings (Figures S2 and S3).

In addition, the samples were characterized by XPS to examine the composition and the oxidation states of the ions in the near-surface region of the catalysts. The Co/Fe surface ratios are summarized in Table 1. The calculation of surface Co/Fe ratios was only possible for Co$_{2.62}$Fe$_{3}$O$_{48}$ to Co$_{2.25}$Fe$_{3}$O$_{48}$ due to the low Fe content of the other samples. Compared with the bulk composition, Co$_{2.62}$Fe$_{3}$O$_{48}$ exhibits a Co-enriched surface, while the samples with higher Co content show the opposite trend with slightly Fe-enriched surfaces.

The Co 2p and Fe 2p XP spectra are shown in Figure 3 and Figure S4a–b. The Co 2p spectra consist of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks together with the respective shake-up satellites. Co$_{2.62}$Fe$_{3}$O$_{48}$ is expected to contain only Co$^{2+}$, whereas the other samples are expected to contain mixed Co$^{2+}$/Co$^{3+}$ oxidation states. Generally, an intense shake-up satellite is observed for Co$^{2+}$ around 786 eV, while Co$^{3+}$ exhibits a weak satellite around 790 eV.[25–27] The oxidation states can be distinguished by comparing the intensity of the shake-up satellites and the splitting (ΔE) of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks.[28,29] Anantharamaiah et al.[29] suggested ΔE between 15.7 and 16.1 eV for samples with higher Co$^{2+}$ amounts and ΔE between 15–15.4 eV for samples containing more Co$^{3+}$. The intense shake-up satellite and the ΔE of 15.6 eV (Table 1) indicate that Co$_{2.62}$Fe$_{3}$O$_{48}$ predominantly contains Co$^{2+}$. The other samples show the typical spectra of spinels containing mixed Co$^{2+}$/Co$^{3+}$. The increased ΔE of Co$_{2.25}$Fe$_{3}$O$_{48}$ indicates an increased amount of Co$^{3+}$ compared with the samples with higher Co contents. The Fe 2p spectra display the 2p$_{3/2}$ and 2p$_{1/2}$ peaks as well as the shake-up peaks. The shake-up peaks of the 2p$_{1/2}$ level are not shown because of the interference with the O KVV Auger transitions (Figure S4b). The Fe 2p peaks show only low intensities for Co$_{2.25}$Fe$_{3}$O$_{48}$ to Co$_{2.62}$Fe$_{3}$O$_{48}$ due to the low Fe content, rendering the interpretation of the oxidation state impossible. Nevertheless, features typical for Fe$^{3+}$ are observed for the other samples with the main Fe 2p$_{3/2}$ peak at around 711 eV and a low-intensity shake-up peak at around 718.8 eV.[30] Furthermore, the 2p$_{1/2}$ peak would be shifted to lower binding

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**Table 1.** Specific surface areas, nominal, and surface Co/Fe ratios as well as ΔE of the Co–Fe-based spinel samples.

| Composition | Nominal Co/Fe | Surface Co/Fe$^{[i]}$ | ΔE$^{[ii]}$ [eV] | Specific surface area [m$^2$g$^{-1}$] |
|-------------|---------------|-----------------------|----------------|-----------------------------------|
| Co$_{2.91}$Fe$_{3}$O$_{48}$ | 0.5           | 0.8                   | 15.6           | 178                              |
| Co$_{2.25}$Fe$_{3}$O$_{48}$ | 3             | 1.8                   | 15.3           | 137                              |
| Co$_{2.82}$Fe$_{3}$O$_{48}$ | 7             | 5.3                   | 15.0           | 129                              |
| Co$_{2.62}$Fe$_{3}$O$_{48}$ | 16            | 11.8                  | 15.0           | 128                              |
| Co$_{2.25}$Fe$_{3}$O$_{48}$ | 32            | n. d.                 | 15.0           | 125                              |
| Co$_{2.62}$Fe$_{3}$O$_{48}$ | 64            | n. d.                 | 15.0           | 128                              |

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Figure 2. TEM images of Co$_{2.91}$O (a), Co$_{2.25}$Fe$_{3}$O$_{48}$ (b), and Co$_{2.62}$Fe$_{3}$O$_{48}$ (c).
energies around 709.5 eV showing a shake-up peak at ~715 eV if the compounds contained mainly Fe$^{3+}$.\cite{29}

Budiyanto et al.\cite{24} further investigated the samples by extended X-ray absorption fine structure (EXAFS), Raman spectroscopy, X-ray emission (XES), and high-energy resolution X-ray absorption spectroscopy (HERFD-XAS). EXAFS and Raman spectra indicated disordering of the Co$^{3+}$–O bonds as well as increased amounts of Co$^{3+}$ with increasing Fe incorporation. A small increase in the overall spin state of Co ions was observed by XES for the mixed Co–Fe spinel oxides. HERFD-XAS showed that Fe preferentially occupies octahedral sites at low Fe loadings and the ratio of Co$_{12}$ to Co$_{12}$ increased. Furthermore, a small relative increase of Co$^{3+}$ was observed for the Fe-containing spinel oxides compared with pure Co$_{12}$O$_{4}$ which could be due to the phase mixture of Co$_{12}$O$_{2}$ and CoFe$_{2}$O$_{4}$ phases as shown by Rietveld refinement.\cite{24} The decrease of the overall oxidation state of the Co cations upon the incorporation of Fe is consistent with the XPS measurements performed in the present study.

Influence of Co substitution on catalytic activities

The mesostructured Co–Fe-based spinel catalysts were applied in the aerobic oxidation of 2-propanol in the aqueous phase using an autoclave operated in the batch mode. The degrees of conversion were kept below 5%, allowing the direct comparison of the initial catalytic activities of the catalysts (Figure 4a). All catalysts showed a linear increase of conversion as a function of the time. Acetone was found to be the only product under these conditions. The conversion after 4 h gradually increased from 0.4 to 3.8% with increasing Co content. Considering the rather constant specific surface areas of the catalysts, it can be concluded that Co cations are more active than Fe cations in the aqueous-phase oxidation of 2-propanol.

Identification of active sites

To gain further insight into the nature of the active site, the initial reaction rates of 2-propanol oxidation normalized by the specific surface areas were derived using Equation (4)

$$r_0 = \frac{n}{(m \cdot S) \cdot \Delta X/\Delta t}$$  \hspace{1cm} (4)

where $n$ is the initial moles of 2-propanol (mol), $X$ is the conversion of 2-propanol at a certain time $t$ (s), $m$ is the weight of the catalyst (g), and $S$ is the specific surface area ($\text{m}^2\text{g}^{-1}$). The initial reaction rates can be derived from the slope of the conversion-time plots because the reaction rate is constant at low conversion ($<5\%$). The obtained reaction rates are plotted in Figure 4b as a function of the Co/(Co + Fe) ratio of the catalysts. The reaction rate showed an exponential dependence on the Co content of the samples. A strong increase of the reaction rate was observed for samples with Co/(Co + Fe) ratios $>0.9$. Hence, even small degrees of Fe substitution into Co$_{12}$O$_{2}$ ($<10\%$) lower the reaction rate very strongly, which was also found in the aerobic oxidation of cinnamyl alcohol, benzyl alcohol, and styrene using the same catalyst series.\cite{16} This observation indicates a superior catalytic activity of Co cations, but the superior activity alone cannot explain the exponential increase of the reaction rate as a function of the Co/(Co + Fe) ratio. Additionally, the overall oxidation state of the Co cations is lowered with increasing Fe content as observed by XPS and XAS measurements.\cite{24} Co$^{3+}$ is assumed to be the most active site in the gas-phase oxidation of CO and 2-propanol.\cite{15,21} Similarly, an increased catalytic activity of Co cations in higher oxidation states could also be valid in the liquid phase. However, single Co$^{3+}$ as the active site cannot explain the exponential increase of the reaction rate for the samples with high Co content (or low Fe content), because the amount of Co$^{3+}$ in these samples is rather similar. This reasoning leads to

![Image](54x352 to 284x775)
the conjecture that the active site may consist of an ensemble of exposed Co cations. Co\(^{3+}\)–O\(^{2-}\)–Co\(^{3+}\) ensembles with nucleophilic anionic oxygen were proposed to be the active site in the gas-phase oxidation of 2-propanol.\(^{[21]}\) Incorporation of Fe would cause a strong decrease of these ensemble sites and, hence, decrease the catalytic activity drastically. To assess the influence of the size of such ensemble sites on the decrease of their number, the normalized number of ensembles only containing Co was calculated and plotted in Figure 4b. The mathematical modelling of the number of active sites as a function of the Co/(Co + Fe) ratio and the number of atoms forming an ensemble is described in the SI. Briefly, the calculation is based on the multinomial distribution and the number of ensembles only containing Co cations is determined from the probability of an ensemble containing only Co cations as a function of the Co/(Co + Fe) ratio and the size of the ensemble. Ensembles consisting of more than six ions already lead to an exponential trend which is similar to the trend of the reaction rate. The trend of the reaction rate is best fitted by an ensemble with 13 atoms. Hence, the active Co ensemble may be larger than six Co atoms.

Nevertheless, the exact number of atoms cannot be determined, since the activity is further affected by long-range effects of the Fe-substitution. The incorporation of Fe induces the transition of Co\(^{3+}\) from low spin to an intermediate spin or hybrid spin state which was also observed by XES.\(^{[31]}\) This transition causes an elongation of Co\(^{3+}\)–O bonds at the catalyst surface.\(^{[31]}\) This change of the electronic structure of the Co ions induced by Fe incorporation may influence the surface reaction by interfering with the dissociative adsorption of 2-propanol or the dehydrogenation of the 2-propoxide intermediate.

In summary, the increasing Co\(^{3+}\)/Co\(^{2+}\) surface ratio suggests Co\(^{3+}\)/Co\(^{2+}\) to be more active than Co\(^{2+}\). The exponential increase of the reaction rate demonstrates that already small amounts of Fe cations affect the catalytic activity of the active sites by altering the electronic structure of Co\(^{3+}\) cations. Therefore, large ensembles of Co\(^{3+}\) which consist probably of more than six cations, are required for 2-propanol oxidation in the liquid phase.

### Kinetic investigations

Being the most active sample among the Co\(_{1-x}\)Fe\(_x\)O\(_4\) series, Co\(_2O\) was further investigated to obtain the kinetic parameters of 2-propanol oxidation. To determine the reaction order with respect to 2-propanol and oxygen, a power law kinetic model was used [Eq. (5)]:

\[
r = k \cdot c_{(CH_3)CHOH}^x \cdot p_{O_2}^y
\]

(5)

The reaction orders are obtained by applying the logarithmic form [Eqs. (6) and (7)]:

\[
\ln(r) = x \cdot \ln(c_{(CH_3)CHOH}) + \text{const}.
\]

(6)

\[
\ln(r) = y \cdot \ln(p_{O_2}) + \text{const}.
\]

(7)

2-Propanol concentration variation experiments were performed according to the standard conditions used for the screening tests with 0.25 and 0.75 wt% 2-propanol aqueous solution (Figure 5). Acetone was the only detected product. Conversion increased with decreasing initial concentrations of 2-propanol. While 3.5 and 3.8% conversion were obtained with 0.75 and 0.5 wt% 2-propanol after 4 h, conversion increased to 4.6% using 0.25 wt% 2-propanol initially. Reaction rates are calculated according to Equation (4) and plotted as a function of the initial 2-propanol concentration in a ln-ln plot (Figure 5b). A reaction order of 0.7 with respect to 2-propanol was determined from the linear fit according to Equation (6).

Likewise, the O\(_2\) pressure variation experiments were carried out at O\(_2\) pressures of 2 and 10 bar. The resulting degrees of conversion are shown in Figure 6a. The selectivity was not affected by the O\(_2\) pressure with acetone being the only product.
product. Similar degrees of conversion were obtained at 5 and 10 bar, while the conversion was slightly lower at 2 bar O₂ pressure. The determined reaction rates were plotted as a function of the O₂ pressure in a ln-ln plot shown in Figure 6b. From the linear fit, the reaction order with respect to O₂ was determined as 0.1 according to Eq. (7).

Furthermore, temperature variation experiments were performed at 140 and 180 °C. The degrees of conversion and yields are plotted in Figure 7a. Compared with the conversion of 3.8% at 160 °C after 4 h, the conversion at 140 °C decreased to 1%, while 10.8% conversion was reached at 180 °C. Acetone was the only product at 140 and 160 °C, whereas acetic acid was also detected at 180 °C. The formation of acetic acid started after 1 h with yields increasing to 0.3% and 0.8% after 2 and 4 h, respectively.

Acetic acid can be formed directly from the oxidation of 2-propanol or by further oxidation of the formed acetone. Delayed formation of acetic acid points to consecutive oxidation of acetone which is further confirmed by probing the oxidation of acetone (Figure S6). During 2-propanol oxidation, CO₂ was detected in stoichiometric amounts to acetic acid within the experimental error. In contrast, the analysis of gaseous products indicates total oxidation forming CO₂ during oxidation of acetone (Figure S7). Nevertheless, CO₂ formation by total oxidation of 2-propanol cannot be fully excluded. Therefore, a reaction scheme is postulated as presented in Scheme 1.

In the first step, 2-propanol is dissociatively adsorbed on the active sites of the catalysts. In a consecutive dehydrogenation step acetone is formed, which is the only reaction product at temperatures below 160 °C. Formed acetone is oxidized at temperatures >160 °C in a consecutive reaction forming acetic acid and CO₂. Possible total oxidation of 2-propanol, acetone, or acetic acid at temperatures >160 °C yields CO₂ and H₂O. Furthermore, the temperature variation experiments are used to determine the apparent activation energy from the Arrhenius equation. The rate constant k is calculated assuming ideal batch reactor behavior [Eq. (8)]:

\[ k = -\ln(1 - X_{\text{OH}}) \cdot t^{-1} \]  

(8)

The apparent activation energy is determined by applying the logarithmic form of the Arrhenius equation yielding 94 (±2) kJ mol⁻¹ for Co₃O₄ (Figure 7b). A comparison with literature data is difficult, since 2-propanol oxidation has not been studied in the liquid phase over Co₃O₄ by now.

Gas-Phase Oxidation

In addition to the catalytic tests performed in the liquid phase, the activity of the Co₃O₄ sample was tested in the gas-phase oxidation of 2-propanol with and without co-feeding water vapor. The typical behavior of Co–Fe-based spinel samples was observed with a low-temperature maximum that is deactivated after the first run and can be regenerated by a temperature-programmed oxidation (TPO) as observed in a previous study (Figure 8a).[21] This deactivation is induced by the adsorption of strongly bound acetate species leading to a reduction of the catalyst surface and coke formation.[22] Approximately 60% 2-
propanol conversion was detected at the low-temperature maximum at 150 °C with acetone being the only product formed indicating an oxidative dehydrogenation pathway. Above 180 °C also total oxidation is observed forming CO₂ with a yield of 25% at 300 °C. Nevertheless, at the maximum temperature acetone is still the main product reaching a yield of 65%. Due to the low heating rate of 1 K min⁻¹, the observed degrees of conversion correspond to quasi steady-state data. Therefore, the apparent activation energy can be derived amounting to 69 (±6) kJ mol⁻¹ (Figure 58). Furthermore, the gas-phase 2-propanol oxidation experiments were also performed with co-feeding of 1.86 % water vapor to build a bridge 70 % conversion being detected at 150 °C. The selectivity at high temperatures is improved by decreasing the CO₂ yield to 20 %, while the acetone yield is increased to 70 %. Furthermore, the overall activity during cooling is higher with water co-feeding compared with the measurement without water co-feeding. Therefore, water vapor improves the deactivation behavior of the Co₃O₄ catalyst as well as the catalytic activity. The apparent activation energy of 89 (±5) kJ mol⁻¹ during heating fits to the value determined in the liquid phase suggesting the same active sites to be present under gas- and liquid-phase conditions when co-feeding water vapor and using water as solvent, respectively. However, during cooling the activation energy is found to be decreased to 68 (±5) kJ mol⁻¹ which is equal to the values determined for the gas-phase experiments without water co-feeding. This observation indicates that after heating to 300 °C the reaction pathway may change presumably due to the partial reduction of the Co³⁺ ions.

Reusability

The catalytic activity of Co₃O₄ is constant as observed for three consecutive runs (X = 3.8 (±0.1) %), indicating no apparent deactivation of Co₃O₄ catalyst after multiple runs. Characterization of the spent catalyst by XRD further revealed that the spinel structure remains stable and no by-phase is formed as shown in Figure S9 for Co₃O₄. Co₁.82Fe₀.18O₄, and CoFe₂O₄. Also, the mesostructure is retained as shown by TEM images for Co₃O₄ (Figure S10a) and Co₁.82Fe₀.18O₄ (Figure S10b). In addition, the composition and the elemental distribution of spent CoFe₂O₄ and Co₁.82Fe₀.18O₄ catalyst were investigated by EDX (Figure S11). The elemental mappings of CoFe₂O₄ (Figure S12) and Co₁.82Fe₀.18O₄ (Figure S13) show a uniform distribution of Co and Fe also in the spent catalysts. This observation supports the retained crystalline structure observed by XRD.

Furthermore, the composition of the fresh and spent catalysts determined by EDX (Table S1) are almost identical to their nominal composition, demonstrating the excellent stability of the catalyst and the absence of leaching of Co or Fe during the reaction. Although deactivation is present in the gas phase with and without vapor co-feeding even at the low-temperature maximum at 160 °C (Figure S13), deactivation is not observed in the liquid phase. The increased stability in the liquid phase compared with gas-phase conditions is presumably due to the dissolution of inhibiting species in water. In this way, coke
formation is prevented, which is responsible for the deactivation in the gas phase.

Conclusion

A series of mesostructured Co_{1-x}Fe_{x}O_{4} spinel oxides was prepared via the nanocasting route by using SBA-15 silica as a hard template and characterized by XRD, TEM, EDX, and XPS. The oxides have rather similar specific surface areas. All samples are phase-pure spinels as shown by XRD except CoO, FeO, and CoFeO_{2} consisting of a phase mixture of CoO and CoO_{2}. TEM images show that the mesostructure of SBA-15 is retained with agglomerated nanoparticles forming nanowires, but the length and interconnectivity decrease with increasing Fe content. Among these spinel oxides, CoFeO_{2} shows the largest specific surface area and random agglomerates of nanoparticles. XPS results suggest that for Co_{2-x}Fe_{x}O_{4} and CoFeO_{2}, the Co^{3+}/Co^{2+} ratio at the outermost surface is decreased compared with stoichiometric CoO and CoFeO_{2}. The activity of the Co_{1-x}Fe_{x}O_{4} samples applied in the liquid-phase oxidation of 2-propanol increases with increasing Co content revealing a superior catalytic activity of Co cations compared with Fe cations. Further, the increasing Co^{3+}/Co^{2+} surface ratio as shown by XPS suggests Co^{3+} to be more active than Co^{2+}. A strong decrease of the reaction rates is observed for small amounts of Fe (≤10%) suggesting an inhibiting effect of Fe cations on the catalytic activity. Therefore, Co^{3+} ensembles are identified as the active sites. Modeling of the normalized number of active ensemble sites showed that the ensembles presumably consist of at least six Co cations. The apparent activation energy of 2-propanol oxidation over CoO_{2} in the aqueous phase is 94 (±2) kJ mol^{-1} which fits to the gas-phase oxidation with water co-feeding. A lower apparent activation energy without water co-feeding suggests a different chemical state of the active sites leading to a different mechanism in the gas-phase reaction. Furthermore, water co-feeding affects the catalytic activity by improving the conversion at the low-temperature maximum and the selectivity at high temperatures as well as decreasing the deactivation at high temperatures. This enhancing effect of H_{2}O for the oxide catalyst contrasts with the findings in literature for noble-metal nanoparticles. Acetic acid and CO_{2} are detected during 2-propanol and acetone oxidation experiments at 180 °C, indicating a consecutive oxidation of acetone in the liquid phase. The spinel structure, the mesostructure, and the composition are retained after the oxidation reaction in the liquid phase. The high stability of the spinel oxides is also observed in the reusability test using CoO_{2} resulting in a constant conversion for 3 consecutive oxidation runs, presumably due to the dissolution of inhibiting species in water.

Experimental Section

Preparation and Characterization of Co_{1-x}Fe_{x}O_{4} (≤x≤2) Spinels

Cobalt and iron mixed metal oxides with controlled mesostructure were prepared by nanocasting as described in detail elsewhere. Briefly, cobalt and iron nitrates in the desired ratio (Co/Fe ratio = 0.5–64 and only Co) were dissolved in ethanol and impregnated into SBA-15 silica as hard template under constant stirring for 2 h at room temperature. After drying overnight at 40 °C, the composite was then calcined at 250 °C for 4 h. The impregnation procedure was repeated once again, and the final calcination was performed for 4 h at 250 °C and followed by 6 h at 550 °C. Calculated 15% of the pore volume of the SBA-15 silica hard template was occupied by the metal oxide. The hard template was removed by leaching in an aqueous solution of NaOH (2 M) at 70 °C.

Characterization methods

X-ray diffraction (XRD) patterns were recorded in the range from 20–80 ° 2θ with a step size of 0.05 ° with a counting time of 0.6 s using a Bruker D8 Discover diffractometer with a theta-theta geometry equipped with a Lynxeye-1D detector using CuKα radiation (λ = 1.5418 Å, 40 kV, and 40 mA), where the fluorescence was automatically suppressed. An air scatter aperture above the sample and a motorized aperture were applied in front of the tube in the primary beam path. The powdered samples were deposited on a silicon single crystal to minimize scattering. Measurements were conducted at room temperature and atmospheric pressure.

For Rietveld refinements (performed with TOPAS 6.0 (6.0 ed., Bruker-AXS 2017, p. Karlsruhe), XRD data were collected with a STOE theta/theta diffractometer in Bragg-Brentano geometry (CuKα1 radiation). The diffractometer was equipped with a secondary monochromator and a point detector. Data were recorded at room temperature with a step size of 0.03 ° 2θ and an acquisition time of 20 s per step.

X-ray photoelectron spectroscopy (XPS) measurements were carried out in a SPECS spectrometer with a hemispherical analyzer (PHOBOS 150). The monochromatized MgKα X-ray source (E =...
Liquid-phase oxidation of 2-propanol

Catalytic tests were performed in a stirred stainless-steel autoclave (Parr Instruments 4560). The degrees of conversion were intentionally kept low (<10%) by choosing appropriate reaction conditions, which are preferred for kinetic studies. Typically, 50 mg powder catalyst and 20 mL of 0.5 wt.% 2-propanol aqueous solution were filled into a Teflon liner. The autoclave was purged three times with nitrogen and then pressurized to 5 bar with oxygen. Afterwards, the reactor mixture was heated to 160°C and the reaction was started by adjusting the stirrer to 600 rpm. Liquid samples were taken after appropriate time intervals and were analyzed with an Agilent 7820A GC system equipped with a capillary column (Agilent J&W DB-WAX, 30 m × 0.25 mm × 0.25 μm) and an FID. The inlet temperature was set to 200°C and the detector temperature to 250°C. The measurements were performed with an injection volume of 0.6 μL and a split ratio of 8:1. The oven temperature was 40°C in the beginning and was heated to 160°C with a heating rate of 15 K min⁻¹. The normalization method was used for quantitative analysis. Therefore, several standard solutions of 2-propanol, acetone, and acetic acid with different concentrations were measured by GC. The relative sensitivity factor (RSF) of 2-propanol was set to 1 arbitrarily and the RSF factors of acetone and acetic acid were calculated accordingly. The errors of the measurements were determined by using Gauss law for propagation of error considering the standard deviations of the GC measurements and of the RSF.

Catalytic tests in the gas phase were performed in a glass microreactor set-up equipped with an online micro-GC. The reactor was filled with 100 mg CuO (sieve fraction 250–355 μm). Prior to every catalytic test an TPO experiment was performed as oxidative pretreatment. Therefore, the sample was heated to 300°C with a heating rate of 3 K min⁻¹ in 10% O₂ in N₂ (100 sccm). The maximum temperature was kept constant for 2 h. The catalytic tests were performed in 0.168% 2-propanol/0.195% O₂/N₂ (100 sccm) and with water co-feeding in 0.175% 2-propanol/0.195% O₂/1.86% H₂O/N₂ (100 sccm). Usually, the sample was heated to 300°C with a heating rate of 1 K min⁻¹. The maximum temperature was kept constant for 2 h and, afterwards, the sample was cooled to 60°C with a rate of 1 K min⁻¹.

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Conflict of Interest

The authors declare no conflict of interest.

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