

The Origin of the Support Effect in MgO-Supported Catalysts

MgO is an interesting catalyst support due to its ability to stabilize the metal in unusual oxidation states and to prevent sintering and volatilization (1-5). However, there are numerous examples where the reactivity of the metal is adversely affected when supported on MgO (6-10). In the CO hydrogenation reaction, MgO-supported catalysts exhibit a greater selectivity to long-chained hydrocarbons than SiO₂-supported catalysts (7-10). While this selectivity behavior is similar to that seen on TiO₂ supports, unlike on TiO₂ it is accompanied by a lower reactivity (7). The unusual properties of TiO₂-supported catalysts are believed to be caused by decoration of the metal surface by TiO_x derived from the support and local electronic perturbation, but the origin of the MgO support effect is not well understood.

A number of possible explanations have been proposed to explain support effects. These are the following: (i) alteration of the morphology and surface structure of the metal crystallites by the support, (ii) decoration of the metal surface by species derived from the support, and (iii) electron transfer between the metal and the support leading to altered chemisorptive and catalytic properties for the metal. In an earlier study, we found that despite a tendency by the Ru to wet the support, the overall shape and exposed surface facets for Ru crystallites were similar on both the MgO and the SiO₂ supports (11). This would tend to rule out any influence of crystallite morphology on the MgO support effect. Van der Lee *et al.* (12) have shown that the selectivity of supported Rh for syngas conversion to methanol is greatly improved when the Rh is supported on Mg(OH)₂. This is because

the support appears to stabilize the Rh¹⁺ species responsible for the higher selectivity. Since aqueous impregnation with acidic precursor salts can transform MgO almost completely to Mg(OH)₂ (13), it appeared important to investigate the role of an intermediate Mg(OH)₂ phase on the properties of MgO-supported catalysts. In this paper, we report our observations on the influence of aqueous versus nonaqueous impregnation on the selectivity of supported Ru in the CO hydrogenation reaction.

Puratronic MgO (AESAR, 99.999%) and MgO smoke were used as supports and the metal loading of all catalysts was 2 wt%. Some of the catalysts were supported on Mg(OH)₂ derived from the Puratronic MgO and others on a high surface area MgO obtained by calcining the hydroxide (13). Details of catalyst preparation and characterization are reported elsewhere (14). All catalysts were prepared by wet impregnation using 4 ml of solvent (water or dry acetonitrile) per gram of support. RuCl₃·3H₂O and Ru(III)2,4-pentanedionate [Ru(acac)₃] were used as precursors. Metal surface area was determined by static volumetric chemisorption of H₂. The chemisorption was performed at room temperature and total uptake of H₂ was used as a measure of the surface concentration of Ru atoms, as recommended by Sayari *et al.* (15). Lu and Tatarchuk (16) have reported that chloride contamination can lead to activated H₂ chemisorption on Ru. They recommend performing the chemisorption at 373 K. However, since we used total uptake of H₂, we were unable to detect any increase in H₂ uptake upon performing the chemisorption at 373 K. In view of the good agreement between TEM and chemisorption-derived

TABLE I
Influence of Catalyst Preparation Conditions
on Product Distributions in the CO
Hydrogenation Reaction

Catalyst code and preparation	N_{CO}^a ($\times 10^3$) (s^{-1})	C ₁	C ₂ ^b	C ₂	C ₃ ^b	C ₃	C ₄ ^b	C ₄	C ₅ ⁺	Conv. (%)
RM02a, m1	6.3	54	8.0	3.9	17	6.5	5.0	0.8	4.8	0.7
RM06a, m1	11	66	3.8	4.7	11	3.8	5.3	0.7	4.7	2.6
RM04a, n3	11	88	1.1	5.0	3.3	1.0	0.5	0.9	0.2	1.6
RM08a, n2	11	79	1.8	6.7	6.1	1.7	1.3	1.5	1.9	1.7
RM07a, o3	10	85	4.2	3.5	5.5	0.2	1.2	0.2	0.2	1.1
RM11a, o4	17	52	9.5	2.8	18	5.5	3.5	1.1	7.6	0.6
RM14a, n1	—	90	0.5	4.4	1.8	0.8	0.4	1.1	1.0	1.5
RM15a, n4	—	69	5.1	6.0	7.1	1.3	1.4	2.8	7.3	0.2

Note. Preparation: m, $RuCl_3 \cdot 3H_2O$, aqueous; n, $RuCl_3 \cdot 3H_2O$, non-aqueous; o, $Ru(acac)_3$, nonaqueous. Support: 1, Puratronic MgO (18 m^2/g); 2, high surface area MgO obtained by calcining $Mg(OH)_2$ (200 m^2/g); 3, low surface area MgO cubes (7.6 m^2/g); 4, $Mg(OH)_2$ made from Puratronic MgO (33 m^2/g).

^a Reaction at 523 K, $He: H_2: CO = 6:3:1$, total pressure = 290 kPa.

^b Oiefin.

particle diameters, we concluded that total H_2 uptake measured at room temperature was adequate for determination of the Ru sites. The catalyst activity for CO hydrogenation was measured using a feed stream containing He, H_2 , and CO in the ratio 6:3:1. The total pressure was 290 kPa. Catalyst reactivity was measured after being put on stream for 10 min. The catalyst was purged with H_2 between runs.

Table 1 presents the results for the catalysts used in this study. The turnover frequencies (TOF) for CO consumption reported in Table 1 agree well with those reported by earlier workers (17–20). The activation energy for CO hydrogenation on these catalysts was 90 kJ/mole and comparable to that for silica-supported Ru (14). The data in Table 1 show that while the selectivity of the catalyst for methane formation is dependent on the method of catalyst preparation, the TOF for consumption of CO is rather insensitive to this variable. We found that the variation in the methanation activity of these magnesia-supported catalysts was primarily due to differences in selectivity toward formation of longer-chained hydrocarbons. The methane percentage on catalysts prepared using method

n or o (i.e., nonaqueously) on MgO is comparable to that on silica-supported Ru (14). On the other hand, the catalysts prepared aqueously (method m in Table 1) using $RuCl_3 \cdot 3H_2O$ as the precursor have a lower methane percentage in the product. The major difference between aqueous and nonaqueous impregnation is that during aqueous impregnation, the MgO transforms to $Mg(OH)_2$.

While both MgO and $Mg(OH)_2$ are rather insoluble in water, some of the MgO undoubtedly gets solubilized under the acidic conditions encountered during aqueous impregnation (13). Hence, one may speculate that a decoration of the metal surface by MgO-derived species may occur on those catalysts prepared via aqueous impregnation. In order to verify this hypothesis, we impregnated a pre-reduced Ru/SiO_2 catalyst with an acidic slurry of MgO. However, no selectivity change was observed on this MgO-treated catalyst in the CO hydrogenation reaction. On the other hand, we observed that catalysts prepared using method n or o (i.e., nonaqueously) but using $Mg(OH)_2$ as the support always exhibited a selectivity to methane that was comparable to that of the aqueously prepared catalysts. This suggests that contact of Ru cations with $Mg(OH)_2$ leads, after dehydration and H_2 reduction, to an active Ru surface with altered catalytic properties.

The effect of the MgO support is to yield Ru catalysts that have depressed methanation activities and higher selectivities for longer-chained hydrocarbons. Before concluding that this is a support effect, it is necessary to rule out particle size effects and the influence of conversion. All the data in Table 1 were collected at a constant temperature of 523 K and for a conversion between 0.2 and 2.6%. Previous work shows that overall conversion of CO, at a given temperature, does not affect the distribution of hydrocarbon chain lengths in the product (7, 9, 17). The dispersion of the catalyst has only a minor influence on the hydrocarbon product distribution (17–19).

Kellner and Bell (18) have reported a rapid decrease in the olefin-to-paraffin ratio but only a slight decrease in the probability of chain growth at dispersions in excess of 0.7. Okuhara *et al.* (19), on the other hand, report a slight increase in the methane selectivity at dispersions greater than 0.7. However, in both these studies the influence of dispersion is seen only at dispersions greater than 0.7, well above the dispersions of the catalysts reported in Table 1 (0.042–0.29). Generally, the particle sizes on two catalysts that differ significantly in selectivity (e.g., RM07a and RM11a, or RM14a and RM15a), but prepared from the same precursor, are quite comparable. The precursor used, $\text{Ru}(\text{acac})_3$ or $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, does not affect the catalytic behavior of the Ru in the CO hydrogenation; however, it does affect the Ru particle sizes in the reduced catalyst. The $\text{Ru}(\text{acac})_3$ yields much larger crystallites than the chloride.

In conclusion, we can state that the MgO support effect appears to be related to the existence of the $\text{Mg}(\text{OH})_2$ phase during the catalyst preparation step. It is not necessary that the catalyst be prepared using $\text{Mg}(\text{OH})_2$ since during aqueous impregnation, the MgO can transform to $\text{Mg}(\text{OH})_2$ if highly acidic precursors are used. Some of the variability in the results reported in the literature on MgO-supported catalysts may be due to differences in the extent of transformation of the MgO to $\text{Mg}(\text{OH})_2$ during the catalyst preparation.

The effect of the MgO support on Ru is similar to that of alkali metal promotion in that it leads to suppressed methanation activity and greater selectivity toward longer-chained hydrocarbons. The XPS data of Doi *et al.* (10) show that Ru on MgO is electron rich and has a lower binding energy than Ru supported on SiO_2 or Al_2O_3 and on Ru foil. The IR spectra of CO adsorbed on MgO-supported Ru have a broad feature around 1960 cm^{-1} (21–23) that is very similar to that reported by McClory and Gonzalez (24) on alkali-promoted Ru. Hence, the MgO support effect on Ru may involve the

creation of electron-rich Ru sites and is fundamentally different from that on Rh where the $\text{Mg}(\text{OH})_2$ phase is believed to stabilize Rh^{1+} species (12). Reduction at temperatures greater than 523 K transforms the $\text{Mg}(\text{OH})_2$ back to MgO and leads to lowered selectivity to methanol in syngas conversion on Rh (12). In contrast, all the Ru catalysts reported here were reduced at 673 K and X-ray powder diffraction spectra confirmed that the only phase present was MgO. Since the MgO support effect is evident in catalysts that have fairly large Ru crystallites (2–20 nm in diameter), decoration of the metal surface by MgO-derived species may be responsible. However, the inability to alter the selectivity behavior of a pre-reduced Ru catalyst by impregnation with MgO or by simply grinding the powder with $\text{Mg}(\text{OH})_2$ suggests that neither of these phases is directly responsible for the decoration that may lead to altered catalytic behavior.

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A. D. LOGAN
A. K. DATYE¹

*Department of Chemical and Nuclear Engineering
University of New Mexico
Albuquerque, New Mexico 87131*

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¹ To whom correspondence should be addressed.